PB85-143261

Technical Assistance Document for Monitoring Sulfuric Acid Vapor from Stationary Sources

Engineering-Science, Inc., Durham, NC

Prepared for

Environmental Monitoring Systems Lab.
Research Triangle Park, NC

Jan 85

U.S. Department of Commerce
National Technical Information Service
NTIS

PB85-143261

EPA-600/4-85-005
January 1985

TECHNICAL ASSISTANCE DOCUMENT
FOR
MONITORING SULFURIC ACID VAPOR
FROM
STATIONARY SOURCES

By

William T. Winberry, Jr.

Engineering-Science
501 Willard Street
Durham, North Carolina 27701
(919) 682-9611

EPA Task Officer
Mr. Thomas J. Logan

Contract No. 68-01-6312
Assignment No. 43

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/4-85-005	**2.**	**3. RECIPIENT'S ACCESSION NO.** PB85-143261
4. TITLE AND SUBTITLE Technical Assistance Document for Monitoring Sulfuric Acid Vapor from Stationary Sources		**5. REPORT DATE** January 1985 **6. PERFORMING ORGANIZATION CODE**
7. AUTHOR(S) William T. Winberry, Jr.		**8. PERFORMING ORGANIZATION REPORT NO.**
9. PERFORMING ORGANIZATION NAME AND ADDRESS Engineering Science 501 Willard Street Durham, NC 27701		**10. PROGRAM ELEMENT NO.** **11. CONTRACT/GRANT NO.** 68-01-6312
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Monitoring Systems Laboratory Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, NC 27711		**13. TYPE OF REPORT AND PERIOD COVERED** Technical Assistance Report **14. SPONSORING AGENCY CODE** EPA/600/08

15. SUPPLEMENTARY NOTES

16. ABSTRACT

When fuels containing sulfur are burned, almost quantitative formation of sulfur dioxide (SO_2) occurs. As much as 5-8% of the sulfur dioxide emitted may be converted to sulfur trioxide either by atomic oxygen in the combustion zone or by efficient catalysis of heavy metal contaminants in the fuel oil. At moisture levels above four percent and temperatures below 300° F (149°C), theoretical models indicate that the sulfur trioxide quickly combines with the water vapor present to form sulfuric acid vapor.

The composition and concentration of the chemical species emitted are influenced by fuel characteristics, boiler design and operation, and emission controls. It is precisely this combination of emissions of different species of sulfates that has hindered the characterization and measurement of sulfuric acid vapor from combustion sources.

This document describes the different types of monitoring principles with their advantages and limitations. Evaluation of different monitoring techniques--both laboratory and field evaluation--are included in the document. Also included is a section dealing with generating known concentration of sulfuric acid vapor used in evaluating monitoring techniques.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Sulfuric Acid Source Emissions Measurement Methods Monitoring Methods		

18. DISTRIBUTION STATEMENT	**19. SECURITY CLASS** *(This Report)*	**21. NO. OF PAGES** 150
	20. SECURITY CLASS *(This page)*	**22. PRICE**

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

DISCLAIMER

This information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Contract No. 68-01-6312, Work Assignment No. 43, to Thomas Logan of the Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina. It has been subject to the Agency's peer and administrative review and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not necessarily reflect Agency policy.

ACKNOWLEDGMENTS

Engineering-Science expresses appreciation to Thomas Logan and William Mitchell of the Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, for their active interest in the project, timely suggestions, and review of the report. Appreciation is also expressed to Dr. Alan J. Senzel for his editorial and technical review. In particular, appreciation is given to Joyce Warren for her patience in typing and editing this manuscript.

TABLE OF CONTENTS

Section	Title	Page No.
	DISCLAIMER	ii
	ACKNOWLEDGMENTS	iii
	TABLE OF CONTENTS	iv
	LIST OF FIGURES	vi
	LIST OF TABLES	viii
	FORWARD	ix
	ABSTRACT	x
1.0	SUMMARY	1-1
2.0	INTRODUCTION	2-1
3.0	BACKGROUND	3-1
	3.1 Historical Perspective	3-1
	3.2 Production of Sulfuric Acid Vapor	3-5
4.0	SULFURIC ACID MONITORING SYSTEMS	4-1
	4.1 Manual Techniques	4-2
	4.1.1 Theoretical Dew Point	4-2
	4.1.2 Deposition Rate Probe	4-5
	4.1.3 Dew Point Meter	4-6
	4.1.4 Federal Reference Method 8	4-9
	4.1.5 Modified Federal Reference Method 6	4-11
	4.1.6 Controlled Condensation System (CCC)	4-17
	4.1.6.1 Brookhaven National Laboratories	4-20
	4.1.6.2 USEPA Industrial Environmental Research Laboratory	4-21
	4.1.6.3 USEPA Environmental Science Research Laboratory	4-25
	4.1.6.3.1 Miniature Acid Condensation System (MACS)	4-26
	4.2 Automated Techniques	4-29
	4.2.1 USEPA Sulfuric Acid Mist Monitor (SAMM)	4-29
	4.2.2 Severn Science Limited SO_3 Monitor (SSL)	4-34
	4.3 Remote Monitoring	4-37
	4.3.1 Remote Optical Sensing of Emissions (ROSE)	4-37
	4.3.2 Tunable Diode Laser	4-43
5.0	SULFURIC ACID MONITORING SYSTEMS - DISCUSSION AND EVALUATION	5-1
	5.1 Manual Techniques	5-1
	5.1.1 Theoretical Dew Point	5-1
	5.1.2 Deposition Rate Probe	5-4

TABLE OF CONTENTS (Contd.)

Section Title Page No.

5.1.3 Dew Point Meter 5-4
5.1.4 Federal Reference Method 8 5-5
5.1.5 Modified Federal Reference Method 6 5-8
    5.1.5.1 Sulfate Artifact Formation on Filtering Devices 5-9
    5.1.5.2 Oxidation of SO_2 Within the Isopropanol Impinger 5-12
5.1.6 Controlled Condensation System 5-12
    5.1.6.1 Controlled Condensation System - Filter Evaluation 5-12
        5.1.6.1.1 General 5-13
        5.1.6.1.2 Out-of-Stack Filtration 5-17
        5.1.6.1.3 In-Stack Filtration 5-19
        5.1.6.1.4 Electrostatic Filtration 5-24
    5.1.6.2 Controlled Condensation System - Collection Efficiency of Goksoyr/Ross Condenser 5-27
5.1.7 Sulfuric Acid Mist Monitor 5-38
5.1.8 Severn Science Limited SO_3 Monitor 5-38
    5.1.8.1 Sudden Large Acid Spikes 5-39
    5.1.8.2 Dissolved Oxygen in 80% Isopropanol 5-39
    5.1.8.3 Reaction Bed 5-39
    5.1.8.4 Isopropanol Light Refraction Characteristics 5-40

6.0 SULFURIC ACID MONITORING SYSTEMS - COMPARATIVE LABORATORY AND FIELD STUDIES 6-1
6.1 Comparative Studies 6-1
    6.1.1 Modified Federal Reference Method 6/Controlled Condensation System/Acid Dew Point Meter 6-1
    6.1.2 Controlled Condensation System/Federal Reference Method 8/Dew Point Meter 6-4
    6.1.3 Severn Science Limited/Sulfuric Acid Mist Monitor/Miniature Acid Condensation System 6-5
    6.1.4 Sulfuric Acid Mist Monitor/Federal Reference Method 8 6-7
    6.1.5 Modified Federal Reference Mthod 6/Controlled Condensation System 6-8

7.0 SULFURIC ACID MONITORING SYSTEMS - ADVANTAGES AND DISADVANTAGES 7-1

8.0 REFERENCES 8-1

APPENDIX A SULFURIC ACID AEROSOL GENERATOR A-1

APPENDIX B SULFURIC ACID MONITORING SYSTEMS SUMMARY OF DRAWBACKS B-1

LIST OF FIGURES

Figure No.	Title	Page No.
Figure 4-0	Sulfuric Acid Monitoring	4-1
Figure 4-1	Phase Diagram of Water-Sulfuric Acid System	4-3
Figure 4-2	Theoretical Dew Point/Sulfuric Acid Curve	4-4
Figure 4-3	Deposition Rate Probe	4-5
Figure 4-4	Acid Deposition vs. Probe Temperature	4-6
Figure 4-5	Acid Dew Point Meter	4-6
Figure 4-6	Acid Dew Point Meter Condensation Surface	4-7
Figure 4-7	Sulfuric Acid Concentration vs. Acid Dew Point	4-8
Figure 4-8	Temperature vs. Rate of Buildup	4-8
Figure 4-9	Federal Reference Method 8	4-9
Figure 4-10	Modified Federal Reference Method 6	4-12
Figure 4-11	Brookhaven Modified Federal Reference Method 6	4-13
Figure 4-12	Controlled Condensation System	4-17
Figure 4-13	Graham and Liebig Condensers	4-18
Figure 4-14	Modified Graham Condenser	4-19
Figure 4-15	Goksoyr/Ross Condensers	4-19
Figure 4-16	Brookhaven Controlled Condensation System	4-20
Figure 4-17	IERL Controlled Condensation System	4-22
Figure 4-18	IERL Probe Configuration	4-23
Figure 4-19	IERL High Temperature Filter Holder	4-24
Figure 4-20	IERL Controlled Condensation Condenser	4-24
Figure 4-21	ESRL Controlled Condensation System	4-25
Figure 4-22	Miniature Acid Condensation System	4-27
Figure 4-23	ESRL Sulfuric Acid Mist Monitor	4-29
Figure 4-24	Sulfuric Acid Mist Monitor Enclosure	4-30
Figure 4-25	SAMM: Compartment #1	4-31
Figure 4-26	SAMM Calibration Curves	4-32
Figure 4-27	SAMM with Heated Cyclone	4-33
Figure 4-28	Severn Science Limited SO_3 Monitor	4-34
Figure 4-29	ROSE System: Van Configuration	4-37
Figure 4-30	ROSE System: Optical System	4-38
Figure 4-31	ROSE System: Light Source - Telescope	4-38
Figure 4-32	ROSE Interferometer	4-39
Figure 4-33	ROSE System: Electronics Receiver Telescope and Interferometer	4-40
Figure 4-34	ROSE System: Tracking Mirror	4-41
Figure 4-35	ROSE System: Typical Spectrum of Sulfuric Acid Vapor	4-42
Figure 4-36	Comparison Spectra: TDL and FT-IR	4-43
Figure 4-37	Tunable Diode Laser Monitoring of Sulfuric Acid	4-44
Figure 5-1	Variation of Dew Point with Varying Water Vapor Concentration	5-2
Figure 5-2	Theoretical Dew Points Curves Based on Partial Pressure Calculation of Sulfuric Acid Vapor	5-3

LIST OF FIGURES (Contd.)

Figure No.	Title	Page No.
Figure 5-3	Field Studies Involving Sulfate Distribution in the Controlled Condensation System	5-19
Figure 5-4	Modified Federal Reference Method 5	5-20
Figure 5-5	Modified Federal Reference Method 17	5-20
Figure 5-6	Relative Percent Weight Loss vs. Temperature of Method 5 Filters	5-22
Figure 5-7	Percent Distribution of Sulfates vs. In-Stack Filter Temperature	5-23
Figure 5-8	Prototype Electrostatic Precipitator	5-24
Figure 5-9	Collection Efficiency of Prototype ESP with Ambient Air Particles	5-25
Figure 5-10	Prototype ESP and SAMM System	5-25
Figure 5-11	Dew Point Range for Water and Sulfuric Acid	5-27
Figure 5-12	Sulfuric Acid Mist Particle Size	5-31
Figure 5-13	Electron Microscopy Enhancement of Embedded Material in Frit	5-32
Figure 5-14	Chemical Analysis of Embedded Material In Frit	5-33
Figure 5-15	Effect of Sampling Rate on Sulfate Distribution	5-34
Figure 5-16	Special Plug for Sulfuric Acid Mist Monitoring	5-35
Figure 6-1	Comparative Studies: Controlled Condensation System and Federal Reference Method 8	6-4
Figure 6-2	Comparative Studies: Inlet	6-6
Figure 6-3	Comparative Studies: Outlet	6-6
Figure 6-4	Comparative Study: Daily Compilation	6-6
Figure 6-5	Comparative Study: Sulfuric Acid Mist Monitor and Federal Reference Method 8	6-7

LIST OF TABLES

Table No.	Title	Page No.
Table 3-1	Sulfuric Acid Mist Monitoring Milestones	3-1
Table 4-1	Modified Federal Reference Method 6 Sample Fractions	4-12
Table 4-2	Brookhaven Modified Federal Reference Method 6 Sample Fractions	4-14
Table 4-3	Absorption Techniques	4-16
Table 4-4	Controlled Condensation System Characteristics	4-28
Table 4-5	Continuous Sulfuric Acid Monitor Characteristics	4-36
Table 5-1	Retention of SO_2 By IPA Impinger	5-6
Table 5-2	H_2SO_4 Capture Efficiency of Greenburg-Smith Impingers	5-7
Table 5-3	SO_3 and SO_4^{-2} Concentrations Measured in the Flue Gases from An Oil-Fired Boiler	5-10
Table 5-4	Artifact Formation in Isopropanol Containing Cationic Species	5-12
Table 5-5	H_2SO_4 Vapor Losses to Filter Media at Various Temperatures	5-14
Table 5-6	Sulfur Dioxide - Sulfuric Acid Mist Challenge Studies	5-13
Table 5-7	Summary of Filter Test	5-15
Table 5-8	Effect of SO_2,H_2O, Sulfuric Acid, and %O_2 on Quartz Fiber Filter	5-16
Table 5-9	Fly Ash Alkalinity Study	5-18
Table 5-10	Comparative Studies: Federal Reference Methods 5 and 17	5-21
Table 5-11	Sulfate Distribution in the Prototype ESP/SAMM System	5-26
Table 5-12	Oxidation of SO_2 to SO_3 Using A Prototype Electrostatic Precipitator	5-27
Table 5-13	Effect of H_2SO_4 Concentration on Capture Efficiency of Goksoyr/Ross Coil	5-28
Table 5-14	Collection Efficiency of Goksoyr/Ross Condenser under Varying Sulfuric Acid and Moisture Concentration	5-31
Table 5-15	Sulfate Distribution and Sampling Rate with Goksoyr/Ross Condenser	5-34
Table 5-16	Total Sulfate with and without Special Glass Wool Plug Holder	5-36
Table 5-17	Acid Collection with Condenser and Special Glass Wool Plug Holder	5-37
Table 5-18	Average Acid Collection with Condenser and Special Glass Wool Plug	5-37
Table 6-1	Sulfuric Acid Mist Monitoring: Comparative Studies	6-2
Table 6-2	Comparative Studies	6-3
Table 6-3	Sulfuric Acid Sulfate	6-3
Table 6-4	Comparative Study: Sulfuric Acid Mist Monitor and Federal Reference Method 8	6-7
Table 6-5	Comparative Study: Modified Federal Reference Method 6 and Controlled Condensation System	6-8
Table 6-6	Comparative Study: Outlet	6-9
Table 7-1	Sulfuric Acid Monitoring Systems: Advantages and Disadvantages	7-2

FORWARD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems; implementation of Agency-wide equality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency, including the Office of Air, Noise and Radiation, the Office of Toxic Substances, and the Office of Enforcement.

Various techniques are available for monitoring sulfuric acid vapor from stationary sources. This document provides an overview of these measuring and monitoring techniques and presents technical information concerning the development and operation of the various sulfuric acid vapor monitors.

Thomas R. Hauser, Ph.D.
Director
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina

ABSTRACT

When fuels containing sulfur are burned, almost quantitative formation of sulfur dioxide (SO_2) occurs. As much as 5-8% of the sulfur dioxide emitted may be converted to sulfur trioxide either by atomic oxygen in the combustion zone or by efficient catalysis of heavy metal contaminants in the fuel oil. At moisture levels above four percent and temperatures below 300° F (149° C), theoretical models indicate that the sulfur trioxide quickly combines with the water vapor present to form sulfuric acid vapor. This newly formed sulfuric acid vapor sorbs onto particulate matter, causing "acid smut." Excess amounts of sulfuric acid vapor or acid smut can cause corrosion within the flue gas ductwork. Once emitted, the condensed sulfuric acid increase can also cause plume opacity of an affected industrial process.

Sulfuric acid in the flue gas can be found as:

(1) A gas phase component at stack temperature and water vapor concentration:

(2) A condensed liquid droplet at temperatures below the acid dew point; or

(3) Absorbed on particulate matter at stack gas temperature. In addition, the free acid may react with metal oxides formed in the combustion flame to yield sulfates as Na_2SO_4, $MgSO_4$, and $Fe_2(SO_4)_3$.

The composition and concentration of the chemical species emitted are influenced by fuel chracteristics, boiler design and operation, and emission controls. It is precisely this combination of emissions of different species of sulfates that has hindered the characterization and measurement of sulfuric acid vapor from combustion sources.

This document has been prepared for the purpose of providing guidance on the selection and use of source emission monitoring techniques for monitoring sulfuric acid vapor from stationary sources. The different types of monitoring principles are discussed with their advantages and limitations. Sections providing statistical evaluation of different monitoring techniques - both laboratory and field evaluation - are included in the document. Also included is a section dealing with generating known concentration of sulfuric acid vapor used in evaluating monitoring techniques.

1.0 SUMMARY

Methods for measuring SO_3 and H_2SO_4 vapor from stationary sources have been investigated. While a search of the literature provided a variety of sampling techniques, no method has yet been accepted as a Federal Reference Method, suitable for all source categories.

The results of this review indicate the following :

- Federal Reference Method 8 is applicable only to the measurement of sulfuric acid at sulfuric acid plants.
- Federal Reference Method 6, or any modifications, will not yield SO_3 and H_2SO_4 vapor concentrations.
- Limited comparisons between the analytical methods for monitoring sulfuric acid from stationary sources are available.
- Use of the controlled condensation system for measuring sulfuric acid is dependent upon the sampling parameters of that system. In particular:
    - Maximum temperature of 271°C to 281°C for probe and filter device preceding the condenser is necessary to assure a minimum H_2SO_4 retention along the sampling train.
    - A sampling rate between 8 and 12 l/min should be maintained for >90% collection efficiency in association with the Goksoyr/Ross coil.
    - Out-of-stack filtration maintained at >271°C is preferred over instack filtration.
- Effect of moisture on acid dew point does not allow a quantitative relationship between acid dew point and sulfuric acid vapor concentration.

- The distinction between sampling isokinetically or nonisokinetically for SO_3 and H_2SO_4 vapor has not been resolved.

- Any method employing absorption or condensation of SO_3 and H_2SO_4 vapor requires a minimum of 4% moisture in the sampling stream.

- Federal Reference Method 5 or a modification thereof will not yield a quantitative value for SO_3 or H_2SO_4 vapor.

- Limited data indicates the Severn Science Limited SO_3 monitor to be a viable approach to monitoring sulfuric acid vapor from stationary sources.

- In its present state, the Sulfuric Acid Mist Monitor (SAMM) is an awkward system not suited for routine field sampling.

- The Remote Optical Sensing of Emissions (ROSE) and the Tunable Diode Laser (TDL) systems have applications for qualitative, but not quantitative, measurements of sulfuric acid vapor from stationary sources.

2.0 INTRODUCTION

When fuels containing sulfur are burned, almost quantitative formation of sulfur dioxide (SO_2) occurs. As much as 8-10% of the sulfur dioxide emitted may be converted to sulfur trioxide either by atomic oxygen in the combustion zone or by efficient catalysis of heavy metal contaminants in the fuel oil. At moisture levels above four percent and temperatures below 300°F (149°C), theoretical models indicate that the sulfur trioxide quickly combines with the water vapor present to form sulfuric acid vapor. This newly formed sulfuric acid vapor sorbs onto particulate matter, causing "acid smut." In addition, excess amounts of sulfuric acid vapor can cause corrosion within the flue gas ductwork. Once emitted, the condensed sulfuric acid increases the plume opacity of the industrial process.

Sulfuric acid in the flue gas can be found as:

(1) A gas phase component at stack temperature and water vapor concentration;

(2) A condensed liquid droplet at temperatures below the acid dew point; or

(3) Absorbed on particulate matter at stack gas temperature. In addition, the free acid may react with metal oxides formed in the combustion flame to yield sulfates as $Na_2(SO_4)$, $MgSO_4$, and $Fe_2(SO_4)_3$.

The composition and concentration of the chemical species emitted are influenced by fuel characteristics, boiler design and operation, and emission controls. It is precisely this combination of emissions of different species of sulfates that has hindered the characterization and measurement of sulfuric acid vapor from combustion sources.

EPA Federal Reference Method 8 was established as a standard procedure for monitoring SO_3 and H_2SO_4 vapor from acid production plants. Because of sulfuric acid plant emissions (low particulate matter), Federal Reference Method 8 is applicable to only that source. Unlike Method 8, those sampling techniques associated with monitoring SO_3 and H_2SO_4 vapor from combustion sources have had the problem of distinguishing SO_3 and H_2SO_4 emissions from particulate sulfate emissions. Many analytical techniques have been developed in order to distinguish between particulate matter and sulfuric acid emissions.

This report will discuss those analytical techniques currently under active use in characterization of sulfuric acid emissions from combustion sources. The weaknesses and strengths of each method will be presented. In addition, data from several investigations will be reviewed indicating relative accuracy and precision of the analytical techniques.

3.0 BACKGROUND

3.1 Historical Perspective

Increased interest in sulfuric acid emissions evolved with the increased use of oil fuel in boilers. Not only was there interest in the cold end corrosion associated with the combustion of a sulfur fuel, but also in the aesthetic effects of their emissions. This interest was reflected as early as 1929, when Johnstone investigated the use of instrumentation to monitor the dew point of a gas stream. Table 3-1 indicates the milestones associated with sulfuric acid mist monitoring tecnniques.

TABLE 3-1

SULFURIC ACID MIST MONITORING MILESTONES

INVESTIGATOR	DATE	DESCRIPTION
Johnstone[1]	1929	First instrumental approach to monitoring dew point of a gas stream.
Goodeve[2]	1936	Use of filter paper to remove sulfuric acid mist from gas stream.
Taylor[3]	1942	Established calibration curves relating acid concentration to dewpoint temperatures.
Knol[4]	1946	Collection of condensed acid by a finger-shaped Grade 4 sintered glass filter.
Flint[5]	1948	First used absorption techniques for monitoring oxides of sulfur from industrial processes employing isopropanol impingers.
Corbett[6]	1948	A phototurbidimetric method for estimation of SO_3 in presence of SO_2.

TABLE 3-1

SULFURIC ACID MIST MONITORING MILESTONES (Cont'd.)

INVESTIGATOR	DATE	DESCRIPTION
Corbett[7]	1951	Further modification of work performed by Flint in 1948.
Corbett,[8] Flint & Littlejohn	1952	Development of a dew point meter for flue gas applications.
Mullen[9]	1959	Calculation of the dew point of flue gas through use of thermodynamic relationships.
Fielder, Jackson & Raashk[10]	1960	Use of air-cooled probe for measuring acid deposition in boiler flue gases.
Knoll[11]	1960	Use of controlled condensation system for monitoring sulfuric acid mist from industrial sources.
Goksoyr & Ross[12]	1962	Application of controlled condensation to monitor sulfuric acid vapor utilizing a modified Graham condenser.
Clark and Childs[13]	1963	Boiler flue gas measurements using a dew point meter.
Lisle and Sensenbaugh[14]	1965	Determination of SO_3 and dew point in flue gas.
U.S. EPA[15]	1971	Federal Reference Methods adopted for determining sulfuric acid mist and SO_2 from stationary sources.
Streiff and Ludwig[16]	1971	First extensive use of a mobile Fourier Transform Infrared (FT-IR) system for air pollution measurements.

TABLE 3-1

SULFURIC ACID MIST MONITORING MILESTONES (Cont'd.)

INVESTIGATOR	DATE	DESCRIPTION
American Society for[17] Testing and Materials	1974	The modified Graham condenser is the basis of an ASTM procedure for monitoring SO_x emissions from industrial sources.
Verhoff and Bancherd[18]	1974	Predicting dew points of flue gases through theoretical curves.
Cheney, Winberry[19] & Homolya	1977	Development of a modified Method 6 procedure for monitoring primary sulfate emissions from combustion sources.
Maddalone and Garner[20]	1977	Construction of a controlled condensation system by TRW for EPA to monitor sulfuric acid vapor.
Land[21]	1977	The theory of acid deposition and its application to the dew point meter.
Dietz, Wieser and Newman[22]	1978	Brookhaven Controlled Condensation System for measurement of combustion flue gas pollutants.
Dietz, Wieser and Newman[23]	1978	Evaluation of a modified Method 6 for flue gas sampling of sulfuric acid.
Pearson & Mantz[24]	1979	Development and application of tunable diode laser instrument for monitoring sulfuric acid vapor emissions.

TABLE 3-1

SULFURIC ACID MIST MONITORING MILESTONES (Contd.)

INVESTIGATOR	DATE	DESCRIPTION
Jain, Blosser,[25] Newport & Oglesby	1979	Evaluation and application of an SO_x measurement procedure as applied to Kraft recovery furnaces.
Cheney and Eaton[26]	1979	Field testing of a continuous sulfuric acid mist monitor (SAMM) at a sulfuric acid plant.
Maddalone, Newton,[27] Rhudy & Statnick	1979	Laboratory and field evaluation of the controlled condensation system for SO_3 measurements.
Cheney and Homolya[28]	1979	Development of a new method for monitoring sulfuric acid emissions using a controlled temperature glass wool plug.
Cheney, Walters & Homolya[29]	1979	Application of an electrostatic precipitator for particle removal in association with a sulfuric acid sampling train.
Herget & Brasher[30]	1980	Application of Fourier Transform Infrared (FT-IR) system to monitoring sulfuric acid emissions at a brick kiln.
Jackson, Hilton & Buddery[31]	1981	Commercially available portable automatic sulfuric acid mist monitor.
Dickson[32]	1982	Comparison of automated and manual sulfuric acid sampling systems.

3.2 Production of Sulfuric Acid Vapor

The production of sulfuric acid begins at the burner tip with the initial formation of SO_2. Flame profile studies and on-site measurements show that SO_2 formation occurs within the primary flame zone at rates comparable to those of other combustion reactions.[33] Formation of SO_2 will proceed in both air-rich and fuel-rich flames at fuel-air ratios up to about 1.4 times stoichiometric. Formation of SO_2 is, therefore, unavoidable, and most of the fuel sulfur will be emitted in this form.

Farther away from the flame, the formation of SO_3 increases while the production of SO_2 decreases. Formation of SO_3 is a function of the mixing temperature and oxygen content. At high temperatures, as in the flame, the amount of SO_3 is less than 0.1% of the total sulfur.[34] As the temperature decreases away from the flame, the relative amount of SO_3 increases to 10% of the total sulfur at about 750°F. This increase is caused by the increased oxygen atom concentration. As the supply of oxygen atoms exceeds equilibrium, SO_3 formation begins by the following equation:

$$SO_{2(g)} + 1/2\ O_{2(g)} = SO_{3(g)}$$

As the oxygen atom population decreases, SO_3 formation ceases and SO_3 concentration remains constant with further cooling. Consequently, the final level of SO_3 is found to be dependent on O_2 content, rate of cooling, and rate and location of excess air.

Therefore, the gas phase formation of SO_3 is directly related to chemical kinetics and surface catalytic activity. The kinetics of flame chemistry have been examined and documented in recent years.[35,36] The various reactions considered include:

$$\begin{aligned}
SO_2 + O + M^* &\longleftrightarrow SO_3 + M\\
SO_3 + O &\longleftrightarrow SO_2 + O_2\\
SO_2 + O &\longleftrightarrow SO_3\\
SO_3 + H &\longleftrightarrow SO_2 + OH\\
SO + O_2 + M &\longleftrightarrow SO_3 + M\\
SO_3 + H_2 &\longleftrightarrow SO_2 + H_2O\\
SO_2 + NO_2 &\longleftrightarrow SO_3 + NO
\end{aligned}$$

[SO_2 = sulfur dioxide; SO_3 = sulfur trioxide, O = atomic oxygen; H = atomic hydrogen; O_2 = oxygen; H_2 = hydrogen; NO_2 = nitrogen dioxide; m = metal ions]

During the combustion of a fossil fuel, the small fraction (1%-5%) of the sulfur that is oxidized to SO_3 by the above reactions can produce a concentration of 5 ppm to 50 ppm in the flue gas as SO_3. This conversion is dependent upon such variables as sulfur content, excess air, and combustion temperature. Further reaction of the SO_3 formed into sulfuric acid vapor or droplets can be initiated by homogeneous gas phase reaction, with subsequent clustering reactions leading to formation of acid droplets.[37]

The droplets can be produced by a three step process:

1. Catalytic oxidation of SO_2 by vanadium and iron:

   $SO_{2(g)} + 1/2\ O_{2\ (g)} \xleftrightarrow{V,Fe} SO_{3\ (g)}$

   The gas phase oxidation of SO_2 to SO_3 is assumed to be rate-determining step in the production of H_2SO_4.

2. Reaction of SO_3 with water to form H_2SO_4:

   $SO_{3(g)} + H_2O_{(g)} + \xleftrightarrow{M} H_2SO_{4(g)}$

   At temperatures below 400°F, essentially all the SO_3 present is converted to H_2SO_4. At this temperature and below the acid dewpoint temperature, the formation of H_2SO_4 occurs rapidly. (M = metal)

3. Clustering of H_2SO_4 and H_2O molecules:

   $H_2SO_4 + x(H_2O) \longrightarrow (H_2SO_4)(H_2O)_x \longrightarrow$ cluster

   $(H_2SO_4)\ (H_2O)_x + H_2O$ particles $\longrightarrow$ Larger particles

In summary, the formation of sulfuric acid in the vapor or droplet state can be affected by the following boiler parameters:

Boiler Parameter	Status	Sulfuric Acid	Metal Sulfate Species
Furnace O_2	Increase	Increase	Increase
Fly ash recirculation	Increase	Decrease	Unknown Effect
Sulfur in oil	Increase	Increase	Unknown Effect
Vanadium in oil	Increase	Increase	Unknown Effect
Other metals in oil	Increase	Unknown Effect	Unknown Effect

For example, increasing furnace O_2 increases sulfuric acid and metal sulfates. Increasing vanadium content in the fuel oil has a direct effect on catalytic activity, increasing sulfuric acid and metal sulfate emissions.

The parameters shown to have the most effect on sulfuric acid emissions were furnace oxygen, flyash recirculation, fuel oil sulfur and vanadium content.[38] Formation of metal sulfates (MSO_4) was primarily governed by furnace oxygen and by the vanadium content of the fuel; i.e., with little or no vanadium in the fuel, MSO_4 remains constant and independent of furnace O_2.

4.0 SULFURIC ACID MONITORING SYSTEMS

Over the years, a number of systems have been developed to detect the presence of sulfuric acid in a flue gas stream. These systems can be divided into three major categories, as shown in Figure 4-0.

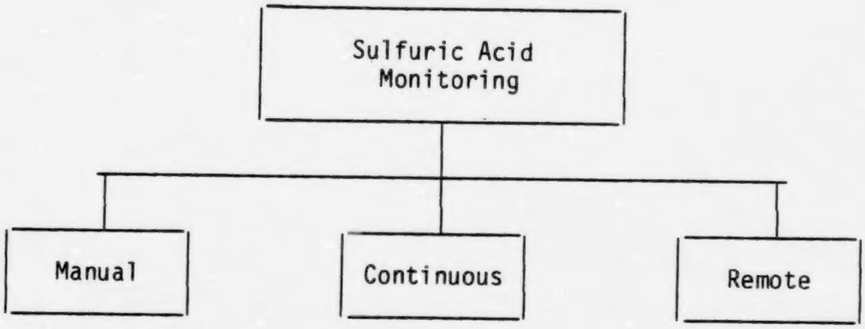


Figure 4-0. Sulfuric Acid Monitoring

Manual systems were the first used to monitor sulfuric acid emissions. Increased technical demands and improving instrumental analysis allowed the development of continuous emission monitoring techniques. Most recently, remote monitors, which can measure plume pollutant concentration as they exit the stack, have been used in sulfuric acid monitoring. This section will examine the techniques used in all three categories of sulfuric acid monitoring.

4.1 Manual Techniques

4.1.1 Theoretical Dew Point

The first analytical techniques associated with sulfuric acid emissions involved determining the acid dew point of the gas stream. It was believed that a correlation existed between the acid dew point and sulfuric acid concentration in the flue gas. As previously described, the formation of SO_3 in the stack gas occurs by the following equation:

$$SO_{2(g)} + 1/2\ O_{2(g)} \longrightarrow SO_{3(g)}$$

The production of SO_3 is temperature dependent; formation of SO_3 at elevated temperature of 1000°F (538°C) is not favored.[39] This is typical of third order reactions. It has long been understood that to reduce deposition and corrosion in oil-fired boilers, one simply reduces excess air levels to a point of optimal combustion. As early as 1963, boiler operations discovered by controlling the fuel-air ratio, the percent excess oxygen could be lowered to 0.2%, thereby reducing fouling and excess corrosion.

Once sulfur trioxide is formed, it will react immediately with any water vapor present in the stack gas to form sulfuric acid by the following equilibrium equation:

$$SO_{3(g)} + H_2O_{(g)} \xrightarrow{T} H_2SO_{4(g)}$$

The amount of sulfuric acid produced is not only dependent upon the amount of water vapor present in the stack gas, but also the temperature of the stack gas. Nearly all of the SO_3 combines with the water vapor when the stack gas temperature is below the boiling point of sulfuric acid, or about 327°C (620°F).

Below 327°C, the sulfuric acid in the vapor stage will begin to condense from the flue gas and deposit on cold surfaces as liquid droplets of sulfuric acid. This temperature of condensation, called the dew point temperature is generally between 93°C (200°F) and 149°C (300°F). The following empirical equation relates the sulfur trioxide concentration and water vapor concentration to the dew point temperature of the gas[40]:

$$1000/T =$$

$$2.2276 - 0.02943 \ln p_{H_2SO_4} - 0.0858 \ln p_{H_2SO_4} + 0.0620 (\ln p_{H_2O})(\ln p_{H_2O}),$$

where T is the dew point in °K and p_{H_2O} and $p_{H_2SO_4}$ are the partial pressures of H_2O and H_2SO_4, respectively, in mm Hg.

This equation, demonstrating the relationship between water and sulfuric acid, can be presented graphically, as shown in Figure 4-1. The dew point is defined as that temperature at which the liquid condensing is in equilibrium with the gas phase immediately above that liquid. Referring to Figure 4-1, note that a solution of sulfuric acid of composition (c), when heated to temperature (a), will change from a liquid state to a gas state. However, the acid and water do not boil off in the same proportion. The resulting composition of the vapor is given by point (b). A vapor of composition (b), when cooled to temperature (a), will condense to a liquid of composition (c). The dew point of the binary system is temperature (a). One can see from this diagram that a small amount of sulfuric acid in the vapor stage condenses to a concentrated solution in the liquid stage when the dew point temperature is reached.

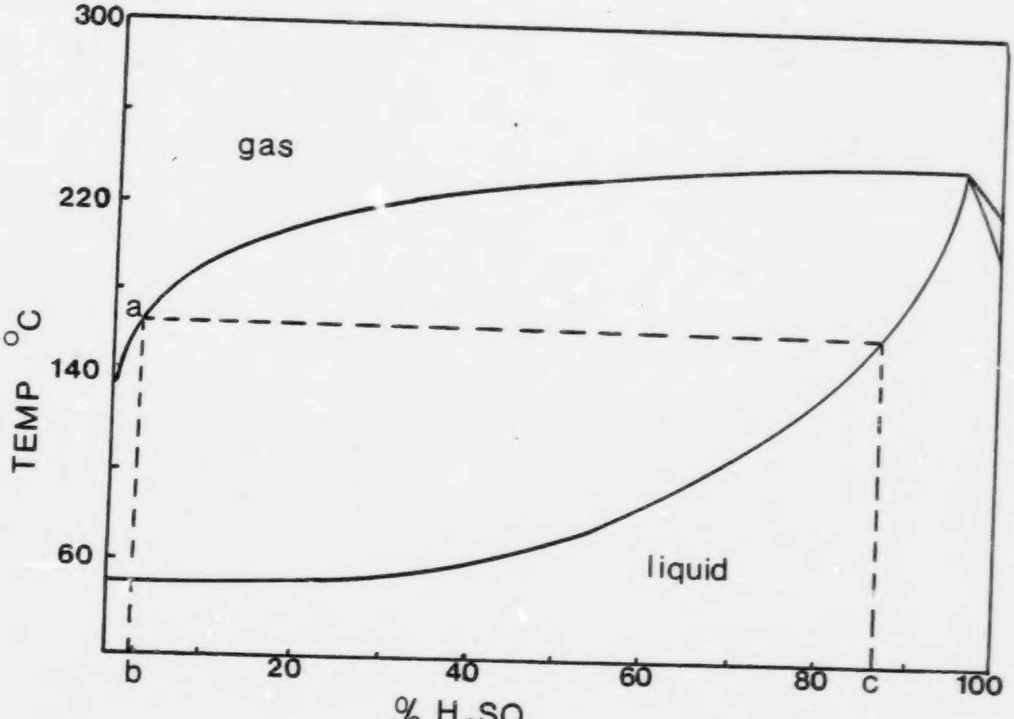


Figure 4-1. Phase Diagram of Water-Sulfuric Acid System

In 1959 Muller developed a theoretical curve displaying the relationship between dew point, sulfuric acid concentration, and water vapor concentration for a gas stream containing 10% water vapor. Other theoretical curves can be constructed depending upon the water vapor content of the gas stream.

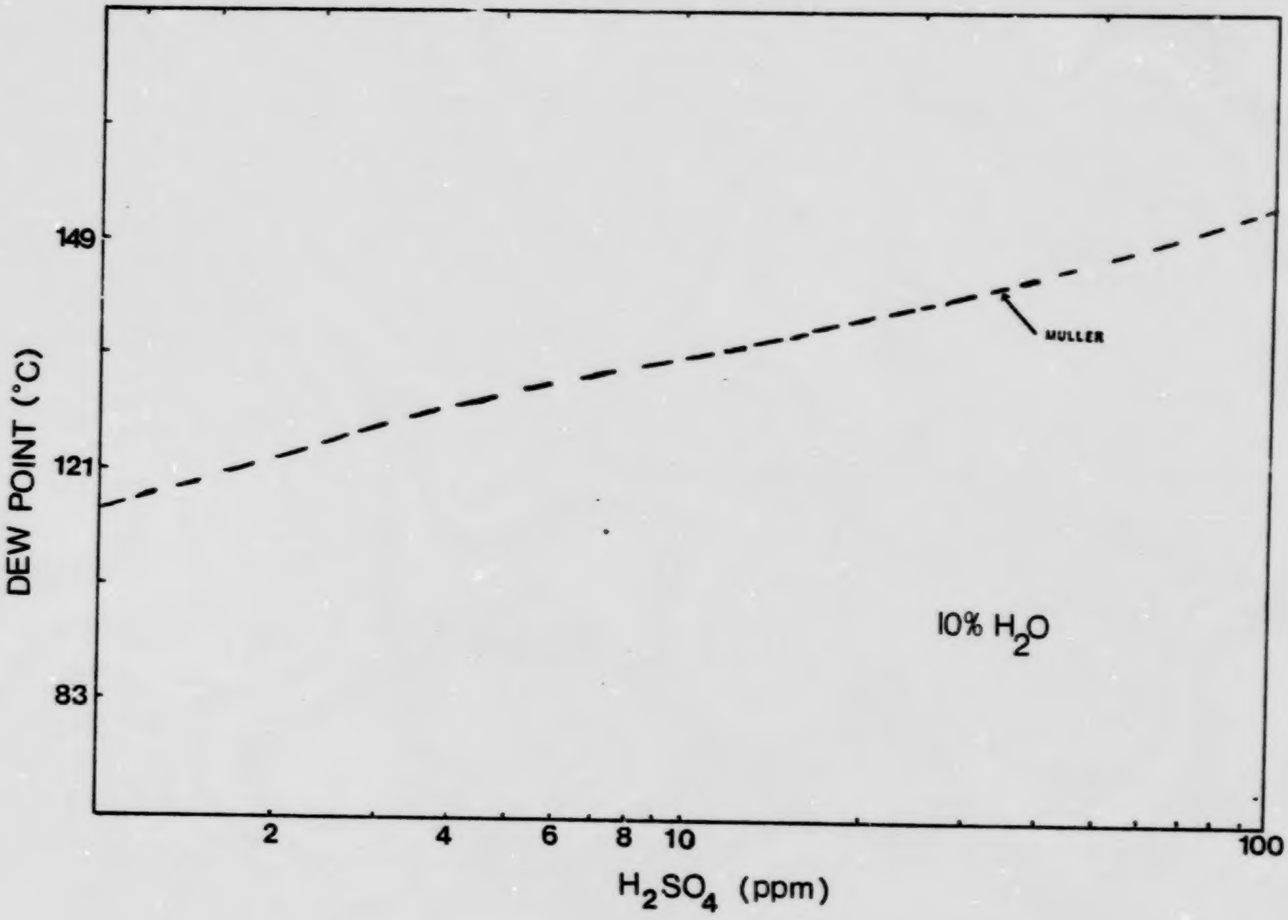


Figure 4-2. Theoretical Dew Point/Sulfuric Acid Curve

Information contained in Figure 4-2 can be used to predict the acid dew of the gas stream containing 10% moisture. Other investigators who developed theoretical dew point curves include Abel[41], Muller[42], and Bancherd and Verhoff[43].

Over the years, several systems have been used to detect the presence of sulfuric acid, its deposition rate, and its dew point. The earliest system used to determine the sulfuric acid concentration in a flue gas stream was termed a deposition rate probe.

4.1.2 Deposition Rate Probe

The deposition rate probe[44] is a constant temperature probe upon which acid is deposited by maintaining the probe below the acid dew point. Figure 4-3 displays a typical deposition rate probe.

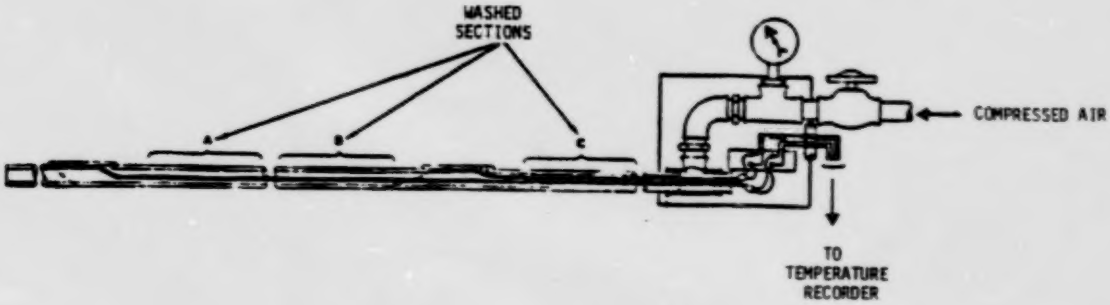


Figure 4-3. Deposition Rate Probe

The probe is divided into sections, each section containing a thermocouple. The probe is inserted into the gas stream, where cool air flows through it. Air flowing through the probe is heated by the flue gas so that each section is progressively warmer. Acid deposits on the cooler surfaces, and after a sufficient time, the probe is withdrawn and each section is washed with distilled water. The catch is then titrated with standard base to a pH of 4.5 for determination of free acid and to a pH of 9.0 for total acid. From the amount of acid deposited, the total surface area, and the exposure time, a deposition rate as a function of temperature can be calculated (Figure 4-4). From this information, a dew point temperature can be extrapolated, as indicated by Point A on the Deposition Rate Probe Curve.

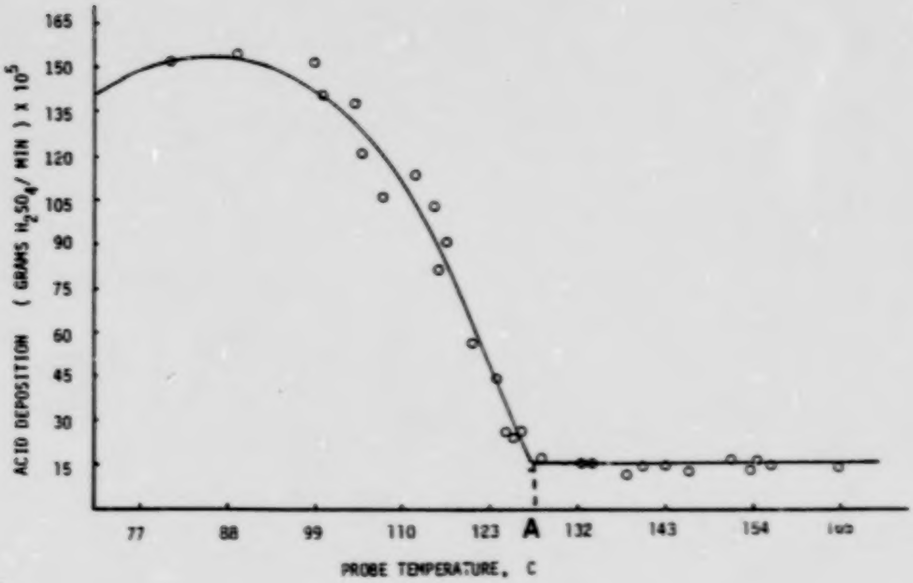


Figure 4-4. Acid Deposition vs. Probe Temperature

Typically, results are reported as g $H_2SO_4/m^2/hr$ at the specific section temperature. In addition, samples can be further analyzed to determine specific pollutants.

Deposition rate probes normally are exposed for periods of hours or days. Acid deposition is directly proportional to time, so test length is not important; however, this method is not reliable for periods of less than one hour. Consequently, a dew point meter was developed to help the boiler operator determine dew point faster.

4.1.3 Dew Point Meter

The dew point meter was modernized by the British Coal Utilization Research Association[45] around 1948. The dew point meter is essentially a control box and a stainless steel probe with a glass thimble embedded in the end, as shown in Figure 4-5, and described further by Flint.[46]

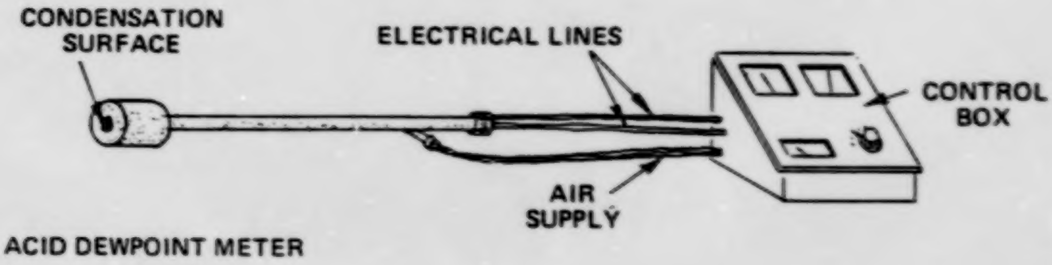


Figure 4-5. Acid Dew Point Meter

Within the glass thimble is a set of platinum-rhodium thermocouples whose junction is fused into the glass. This junction is part of a conductivity cell whose other electrode is a concentric platinum ring, also flush with the surface, as shown in Figure 4-6. A separate thermocouple is attached to the outside of the probe to monitor stack gas temperature.

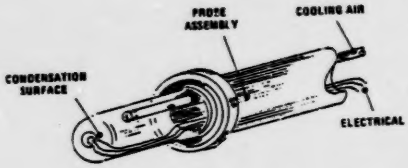


Figure 4-6. Acid Dew Point Meter Condensation Surface

In operation, the probe is inserted directly into the gas stream. A source of clean, dry air is provided to the inside of the probe. The clean, dry air comes into contact with the inside surface of the glass thimble, thus lowering its temperature. As the glass thimble is cooled below the dew point of the stack gas, a film of acid condenses on the outside surface of the thimble. Once a uniform layer of acid is deposited, an electrical circuit is completed by making contact with the pair of electrodes fused into the glass surface. The thin layer of acid is maintained by adjusting the air flow within the probe. The acid dew point (ADT) is defined by the temperature at which this thin layer of acid can be maintained. At the acid dew point, the acid film is in equilibrium; the rate of evaporation and condensation are equal. This dew point temperature is monitored by a thermocouple also fused into the detector surface. Figure 4-7 displays the relationship between sulfuric acid concentration and the acid dew point temperature of a flue gas stream at different water vapor concentrations. The acid dew point of a flue gas stream is also dependent upon moisture concentration, as shown in the following equation:

$$SO_{3(g)} + H_2O_{(g)} \xleftrightarrow{T} H_2SO_{4(g)}$$

Consequently, the acid dew point temperature is moisture-dependent.

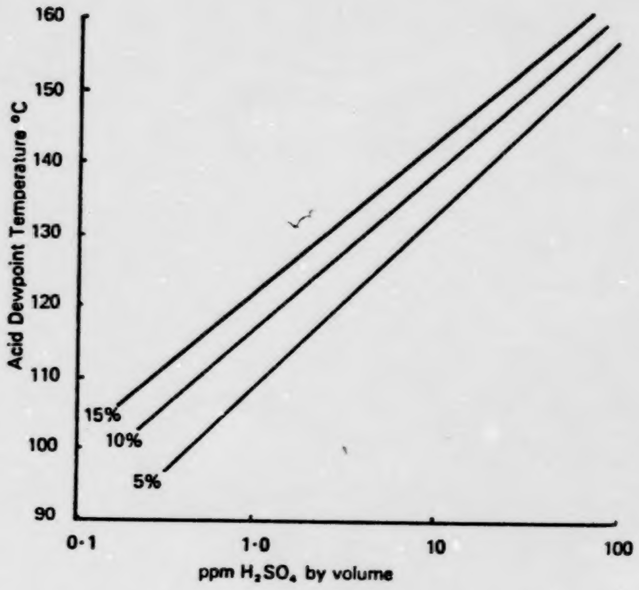


Figure 4-7. Sulfuric Acid Concentration vs. Acid Dew Point

In addition, the corrosion potential of the flue gases can be assessed by measuring the rate of acid buildup (RBU) at temperatures below the ADT.

When the dew point probe is cooled below the acid dew point, acid will build up. If one determines the RBU for several temperatures, it is possible to plot RBU as a function of temperature. RBU is expressed in µ a/min. An RBU less than 100 µa/min indicates low acid concentration, minimal corrosion. Over 500 µa/min is associated with severe corrosion, high acid concentration. Figure 4-8 displays a typical curve showing temperature vs. RBU.

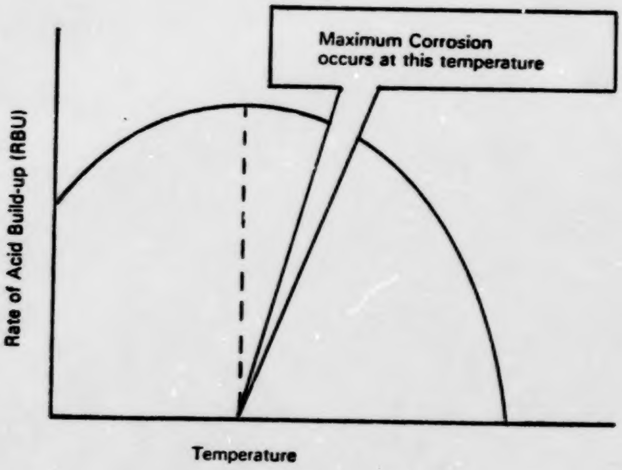


Figure 4-8. Temperature vs. Rate of Acid Buildup

Concurrent with the instrumental development of monitoring sulfuric acid emissions was the development of absorption techniques. Its beginning dates back to 1948 when Flint[11] monitored sulfuric acid mist from combustion sources using 80% isopropanol in an impinger train. This technique became the basis for Federal Reference Method 8, which is used for monitoring sulfuric acid emissions from sulfuric acid plants.

4.1.4 Federal Reference Method 8

The Federal Reference Method 8 sampling system consists of a probe/pitot tube assembly, a condenser containing four Greenburg-Smith impingers, and a metering system containing a pump, a dry test meter, and an orifice meter (Figure 4-9).

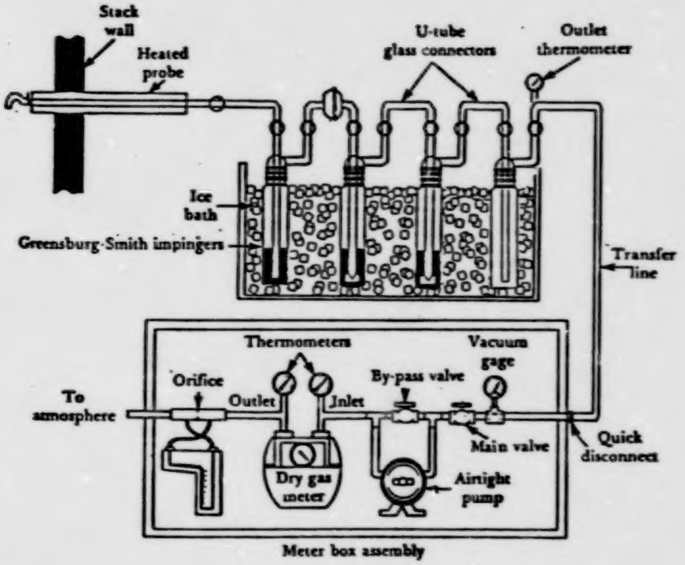


Figure 4-9. Federal Reference Method 8

In essence, the stack gas sample is withdrawn isokinetically from the source through a nozzle, heated borosilicate or quartz probe, and impinger assembly. The probe is maintained at 120°C(248°F) to prevent condensation of sulfuric acid. Since Federal Reference Method 8 was intended for monitoring sulfuric acid emissions from sulfuric acid plants, no heated filter is required to remove particulate matter from the gas stream.

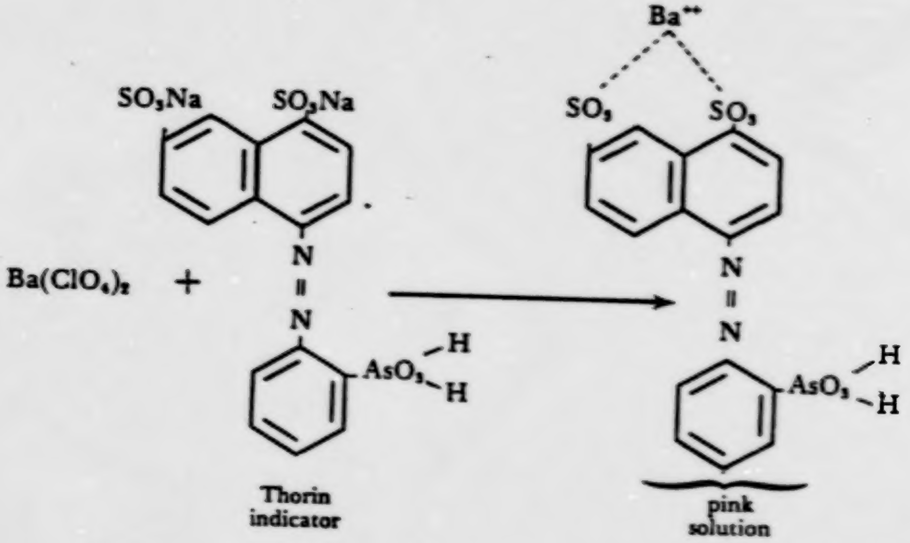
Sulfuric acid is quantitatively removed from the gas stream by being absorbed in the first impinger containing 80% isopropanol (IPA) solution. The IPA abosrbs sulfuric acid but does not absorb SO_2. The SO_2 in the gas stream is removed by the impingers containing hydrogen peroxide (H_2O_2).

Once H_2SO_4 collected, the 80% isopropanol impinger is removed from the sample train and analyzed for sulfate by the barium-thorin titration, as per the following equation:

Sulfate Reaction

$$\mathrm{Ba(ClO_4) + H_2SO_4 \xrightarrow{Thorin} \underbrace{BaSO_4 + ClO_4^-}_{yellow\ solution}}$$

Barium-Thorin Reaction



The amount of sulfate present is directly proportional to the concentration of sulfuric acid in the stack gas.

Because no filter precedes the IPA impinger, the use of Federal Reference Method 8 on fossil fuel-fired boilers is impractical. A sampling system was needed to reduce the interferences of particulate sulfates from the sampling and analytical scheme effectively. A total water-soluble sulfate (TWSS)[47] sampling system was evaluated for monitoring sulfuric acid through modification of Federal Reference Method 6.

4.1.5 Modified Federal Reference Method 6

Federal Reference Method 6 and its modifications are similar to Method 8, and both have been used to sample sulfuric acid emissions from stationary sources. Federal Method 6 employs the same absorption techniques as Method 8; both extract a gas sample through a heated quartz or borosilicate probe fitted with a glass wool plug into a series of midget impingers. The first impinger contains 15 ml of 80% isopropanol (IPA), which abosrbs the sulfuric acid from the gas stream. Since SO_2 is not appreciably soluble in isopropanol, it is absorbed in the next two midget impingers each of which contains 15 ml of 3% hydrogen peroxide (H_2O_2). A fourth dry impinger is inserted before the sampling pump to trap any liquid carryover. To prevent acid mist carryover, a plug of glass wool is inserted between the first and second impinger.

Federal Reference Method 6 is used solely for determining SO_2 emissions. Absorption of SO_2 by the hydrogen peroxide impinger solution occurs by the following mechanism:

$$SO_{2(g)} + H_2O_2 \longrightarrow H_2SO_4$$

The front half of the train containing the probe plug, probe wash, and IPA impinger is discarded. Only the hydrogen peroxide impingers are analyzed for sulfate by the barium-thorin titration.

The Modified Federal Reference Method 6 sampling train involves the same configuration, but the analysis is modified. In practice, the flue gas stream is sampled at a rate of 500 to 750 cc/min to provide a total standard gas volume of approximately 28 liters. After sampling, the probe is immediately removed from the source stream. Any SO_2 retained by the IPA solution in the first impinger is purged by flushing with clean air, at ambient temperature, for a total volume of at least 14 liters. The entire sampling train is then dismantled and analyzed by the barium-thorin titration for sulfate ions. The sulfur species collected and analyzed by Modified Federal Reference Method 6 are indicated in Table 4-1.

TABLE 4-1

MODIFIED FEDERAL REFERENCE METHOD 6 SAMPLE FRACTIONS

Sampling Train Element	Sulfur Species Collected[1]
Probe Plug (quartz or pyrex)	H_2SO_4, MSO_4, SO_3, carbon
Probe Wash	H_2SO_4, MSO_4
Isopropanol Bubbler and Impinger Plug	H_2SO_4
Peroxide Impingers and Dry Impinger	SO_2

[1] H_2SO_4 = Sulfuric Acid; MSO_4 = Metal Sulfates; SO_3 = Sulfuric Trioxide

Following the impinger train is a meter box assembly containing the pump, silica gel, and dry gas meter. The connection between the impinger train and meter box assembly is accomplished by a transfer line. Figure 4-10 displays the complete sampling system.

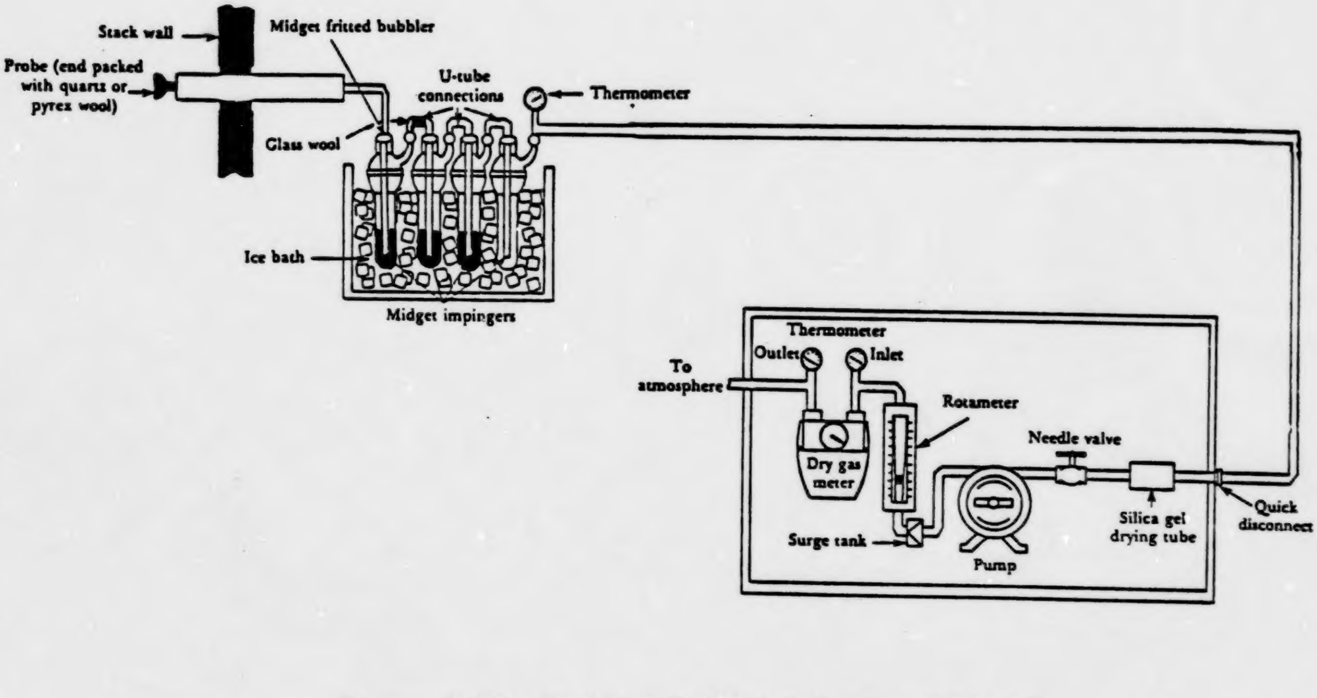


Figure 4-10. Modified Federal Reference Method 6

As discussed earlier, the distinction between Federal Reference Method 6 and Modified Federal Reference Method 6 lies in the components which are analyzed for sulfate. In the Reference Method, only the hydrogen peroxide impingers are analyzed. Consequently, neither Federal Reference Method 6 nor its modification provides a separate sulfuric acid vapor value.

The primary purpose in the design and operation of the Modified Federal Reference Method 6 train is to trap sulfates (sulfuric acid and metalic sulfates) and SO_2 efficiently. Consequently, data reported from this train are typically divided into two groups: total water-soluble sulfates (TWSS) and SO_2.

Brookhaven National Laboratory developed a sampling system capable of monitoring metallic sulfates and sulfuric acid independently. The system[48] employed an in-stack filter to capture metallic sulfates, while allowing the sulfuric acid vapor fraction to pass to the midget impinger system containing 80% isopropanol and hydrogen peroxide. Once again, sulfuric acid is retained in the IPA impinger and impinger filter while SO_2 passes to the hydrogen peroxide impinger. Each fraction is collected separately and analyzed for sulfates by either the barium-thorin titration or ion chromatography. Figure 4-11 displays the sampling system.

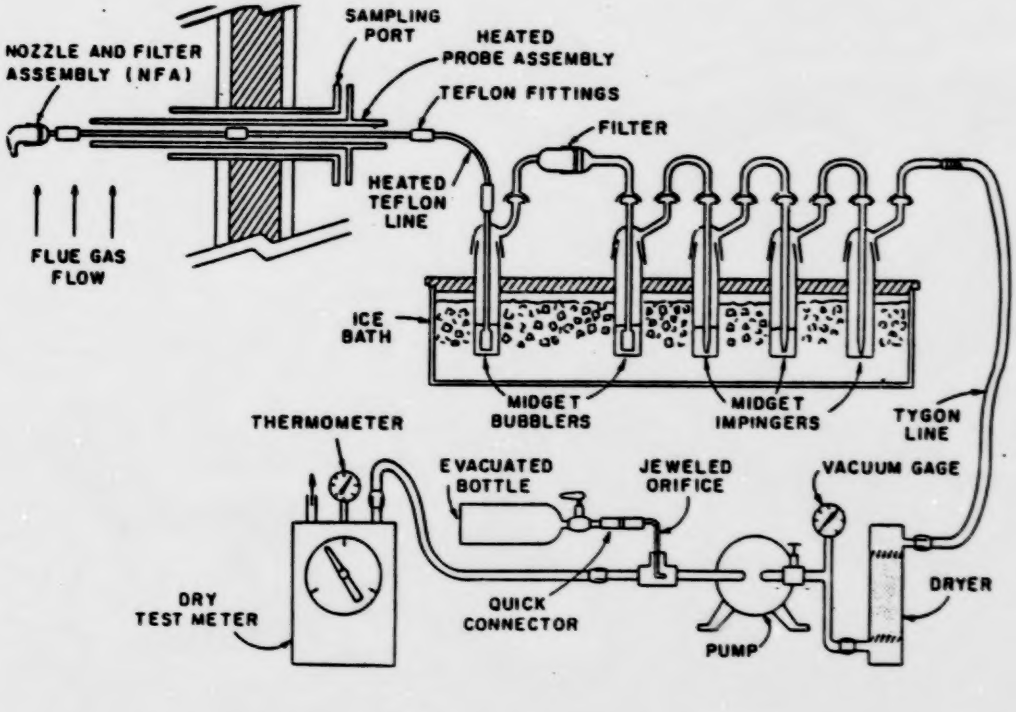


Figure 4-11. Brookhaven Modified Federal Reference Method 6

The nozzle and filter assembly consists of an in-stack nozzle with an inside diameter of 1 mm for isokinetic sampling at 1 l/min or 2 mm for sampling at 0.5 l/min. The flue gas enters the nozzle isokinetically and proceeds to a coarse frit containing a 40 mm diameter quartz fiber filter that has been phosphoric acid-washed and heat-treated to remove organic materials. The metal sulfates are removed by the filter. The sulfuric acid vapor passes down a heated 160°C (320°F) quartz probe to the impinger system. The Brookhaven Modified Method 6 impinger assembly is essentially identical to the Modified Federal Reference Method 6 assembly. The system consists of a series of midget impingers containing an appropriate absorbing solution to scrub out SO_3/H_2SO_4 and SO_2. The first midget bubbler contains 80% isopropanol to trap SO_3 and H_2SO_4. Following the first impinger is a filter assembly used to retain any entrained liquids. The filter assembly contains a heat- and acid-treated quartz fiber filter.

Following the filter assembly is a series of impingers containing H_2O_2 for absorption of SO_2. The fourth impinger is dry to retain entrained liquids, with the fifth impinger contains silica gel for moisture removal. The impingers are immersed in an ice bath. The meter box assembly containing the pump, dry gas meter and other gas metering hardware follows the impinger train.

Those fractions routinely sampled and analyzed by the Brookhaven Modified Method 6 are listed in Table 4-2.

TABLE 4-2

BROOKHAVEN MODIFIED FEDERAL REFERENCE METHOD 6 SAMPLE FRACTIONS

Sampling Train Elements	Sulfur Species Collected[1]
Probe Nozzle and Filter	MSO_4, Carbon
Probe and Wash	MSO_4
Isopropanol Bubbler and Filter	H_2SO_4
Peroxide Impingers and Remaining Impingers	SO_2, H_2O

---

[1] MSO_4 = Metal Sulfates; H_2SO_4 = Sulfuric Acid; SO_2 = Sulfur Dioxide; and H_2O = Water

The primary difference between Brookhaven Modified Federal Reference Method 6 and the Modified Federal Reference Method 6 is that the former samples isokinetically. Sampling isokinetically, allows the user to quantify particulate sulfate emissions as well as sulfuric acid emissions from a source. Additionally, the use of an in-stack, unheated filter, according to Dietz, does not disturb the equilibrium between the particulate sulfates and sulfuric acid vapor as they exist in the stack gas, thus allowing the user to "truly" sample a representative emission for the source.

Table 4-3 summarizes the characteristics of the absorption techniques thus described.

TABLE 4-3

ABSORPTION TECHNIQUES

Sampling System	Federal Reference Method 8	Modified Federal Reference Method 6	Brookhaven Modified Federal Reference Method 6
System Components			
Probe			
o Construction	Pyrex	Pyrex	Pyrex
o Temperature	130°C	130°C	175 - 225°C
Particle Filter			
o Type	-	Bed	Surface
o Size	-	-	40 mm
o Filter Media	-	Pyrex Wool	Quartz
o Temperature	-	Stack Temp.	Stack Temp.
o Location	-	In-Stack	In-Stack
o Pretreated	-	- -	Heat-Treated Phosphoric Acid Wash
o Frit size	-	-	Medium
Sulfuric Acid Collection Device	Greenburg-Smith Impingers	Midget Impingers	Midget Impingers
o Solution	80% IPA	80% IPA	80% IPA
Sampling Rate	Isokinetically	0.500-0.700 lpm	1 lpm or isokinetically
Analytical Techniques			
o Sulfuric Acid	Barium-Thorin	Barium-Thorin	Acid/Base
o Metal Sulfates	-	Barium-Thorin	Ion Chromatography

4.1.6 Controlled Condensation System

The need to distinguish between particulate sulfate and sulfuric acid vapor in a sampling system led to the development of the controlled condensation system.

The controlled condensation system is based upon the selective condensation of sulfuric acid from a gas stream by means of a water cooled condenser. First proposed by Knol[49] in 1960 and further refined by Goksoyr and Ross[50] in 1962, the controlled condensation system remains one of the primary sampling and analytical tools for quantifying sulfuric acid emissions from stationary sources.

The system consists of five major components: probe, high temperature filter device, condensation coil, sampling module, and pumping meter box, as shown in Figure 4-12.

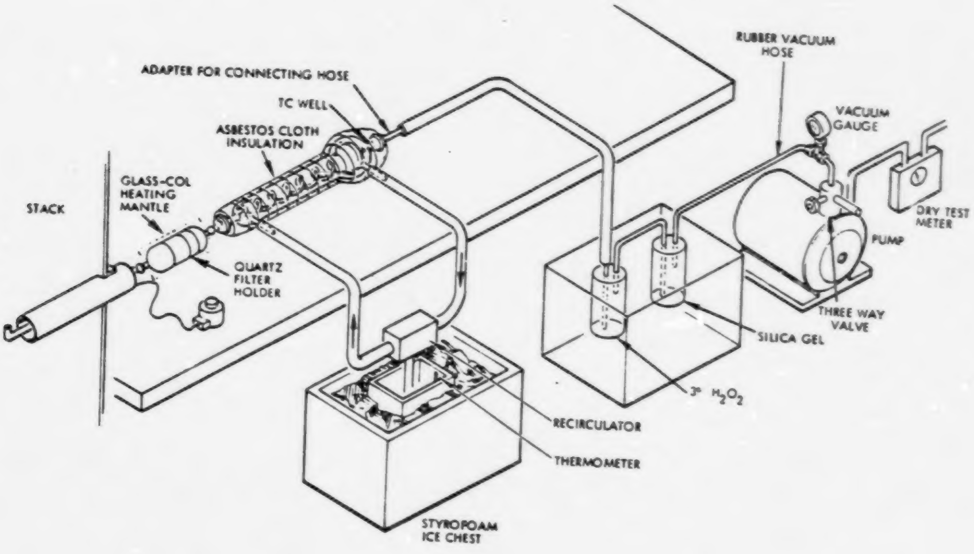


Figure 4-12. Controlled Condensation System

The probe consists of an inner lining of pyrex, quartz, or vycor glass wrapped in nichrome wire to allow heating to 289°C (550°F). The inner lining and heating mechanism are protected by an outer sheath of stainless steel. Attached to the probe assembly, by way of glass ball joint fitting, is a high-temperature quartz filtering device. The filtering device contains a coarse quartz frit upon which the filtering material is supported. To prevent condensation of sulfuric acid on the filter medium, a heating mantle is provided to maintain the filtering system at 289°C (550°F). Following the filtration system is the condenser coil. The condenser is a multiturn glass coil with a medium porosity frit located at the end. The coil and frit are water cooled by an auxiliary water bath to a constant temperature of 60°C (140°F). This temperature is below the acid dew point but above the water dew point of the stack gas.

The earliest condenser used was a Graham condenser. It was chosen over the more popular and common Liebig condenser because its ability to give a much higher rate of condensation for a given surface area (Figure 4-13).

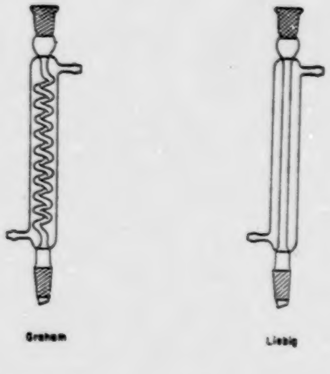


Figure 4-13. Graham and Liebig Condensers

In 1961, H. Goksoyr and K. Ross of the Thornton Research Center applied the Graham condenser to monitoring of sulfuric acid vapor from combustion sources. However, after laboratory evaluation, a sintered glass filter was added to the outlet of the spiral coil to collect any sulfuric acid aerosol that escaped the condenser coil.

The modified Graham condenser, as shown in Figure 4-14, has become the standard device for collecting sulfuric acid vapor in the controlled condensation system. Since its application by Goksoyr/Ross, the modified Graham condenser has been referred to as the Goksoyr/Ross condenser. Figure 4-15 displays several versions of the Goksoyr/Ross condenser in use today.

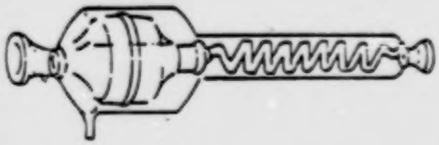


Figure 4-14. Modified Graham Condenser

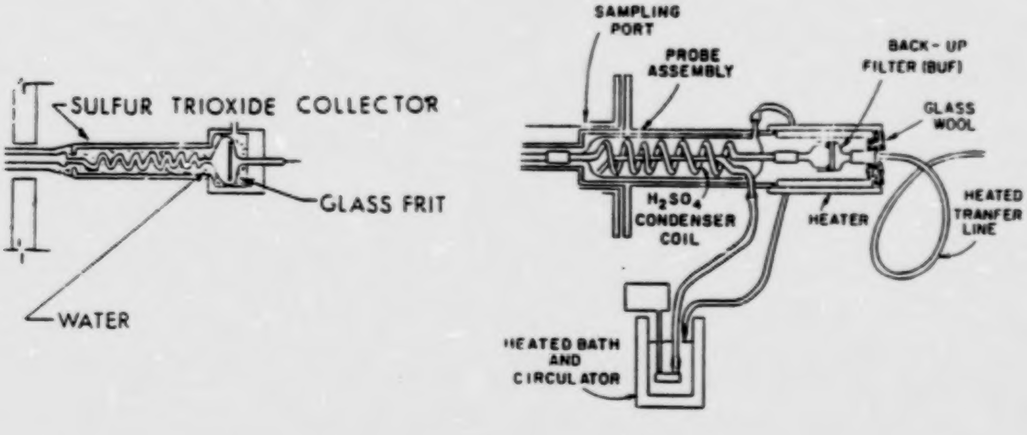


Figure 4-15. Typical Goksoyr/Ross Condensers

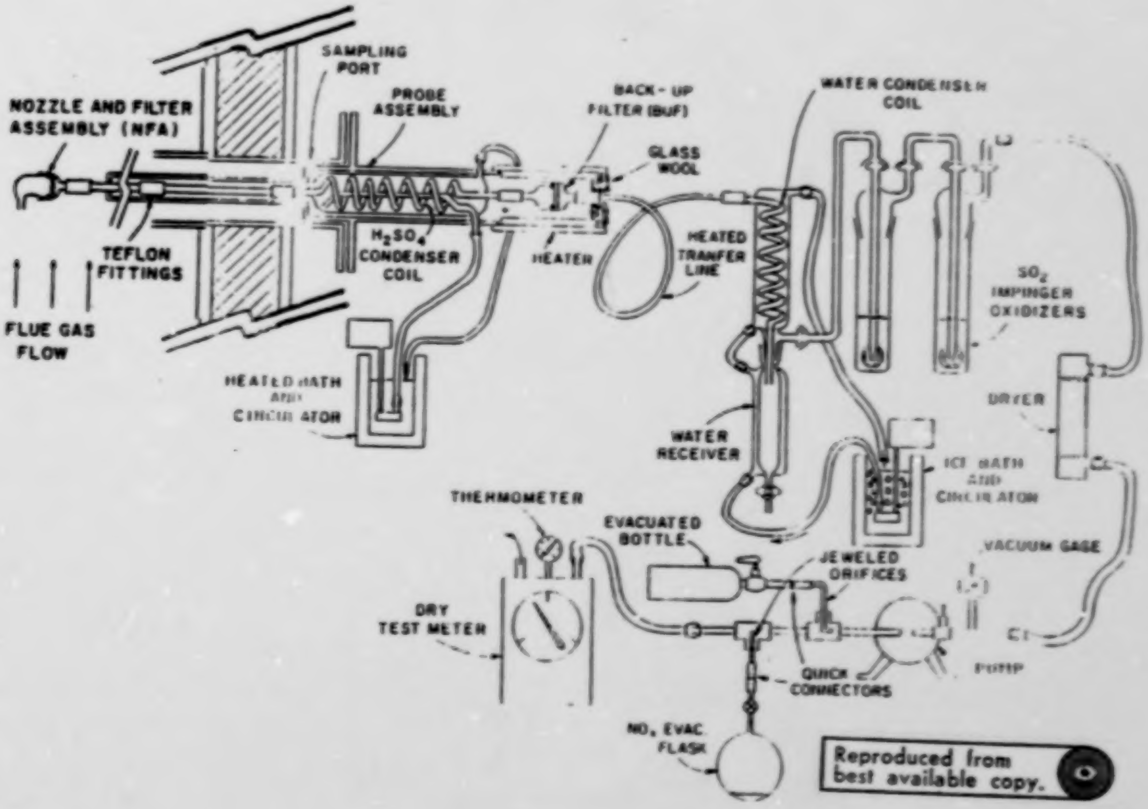
Following the condenser is an ice bath containing a series of Greenburg-Smith impingers. The impingers are used to absorb auxiliary pollutants. An umbilical cord connects to the sampling module, to the meter box assembly containing the pump, to the dry gas meter and to the orifice meter for monitoring sampling rate.

In operation, the probe is inserted into the stack gas, the sample is extracted from the source and the recovered condenser is analyzed for sulfuric acid vapor.

Several versions of the controlled condensation system have appeared over the years.[51,52,53] The main concern has been the ability to distinguish sulfuric acid vapor from particles absorbed with sulfuric acid during sampling. Several approaches have been taken to address this problem.

4.1.6.1 Brookhaven Controlled Condensation System

The ability to distinguish between sulfuric acid mist and metal sulfates in the flue gas has been a major problem associated with all analytical techniques for monitoring sulfuric acid emissions from combustion sources. Brookhaven National Laboratory has developed a method for simultaneous monitoring of particulate sulfate and sulfuric acid mist from combustion sources. The Brookhaven Controlled Condensation System, Figure 4-16, is designed to measure the vapor phase flue gas concentrations of sulfur dioxide (SO_2) and sulfuric acid (H_2SO_4) plus the metal sulfate (MSO_4) particles in the flue gas. In addition, the sampling train has the ability to monitor water vapor (H_2O), oxygen (O_2), carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxide (NO_x), and total suspended particles (TSP).



Reproduced from best available copy.

Figure 4-16. Brookhaven Controlled Condensation System

In operation, flue gas is sampled isokinetically, nominally at 10 l/min, through an unheated in-stack nozzle/filter assembly (NFA) which removes all suspended particles but passes the sulfuric acid vapor. Subsequently, the sulfuric acid vapor is condensed and removed by impaction in the controlled condensation coil. The quartz backup filter (BUF) assures quantitative removal of H_2SO_4. Following the sulfuric acid removal, water is condensed in an ice water-jacketed condensation coil and receiver vessel. Sulfur dioxide is collected by oxidation to sulfate in two Greenburg-Smith impingers, each containing 3% H_2O_2 solution. Other gases are captured in two 0.5 l evacuated flasks located downstream of the impinger system. Total volume of the gas stream extracted is determined by a dry gas meter located on the outlet of the sampling system.

Major differences between the Brookhaven Controlled Condensation System and other controlled condensation systems is the use of an unheated in-stack filter/nozzle assembly rather than an out-of-stack filter assembly. The in-stack filter/nozzle assembly allowed for isokinetic (+ 20%) sampling, thus enabling gravimetric determination of flue gas particulate matter. This cannot be accomplished with other condensation systems. Brookhaven decision to use an unheated filter was based on the assumption that sulfuric acid vapor and particulate fly ash are present in the duct in a dynamic equilibrium and that changing any conditions, such as filter temperature, might adversely shift this balance. With an out-of-stack heated filter assembled, Brookhaven saw potential problems including: 1) irreversible conversion of adsorbed H_2SO_4 into metal sulfates; 2) catalytic conversion of SO_2 into SO_3 and metal sulfates (MSO_4) 3) catching and holding particles on a heated filter could cause further adsorption of H_2SO_4 vapor on those trapped particles.

4.1.6.2 U.S. Environmental Protection Agency (Industrial Environmental Research Laboratory)[54]

Concurrent with the development of the Brookhaven controlled condensation system, U.S. EPA Industrial Environmental Research Laboratory (IERL) was developing their own system to aid in their research projects involving scrubber efficiency studies.

The IERL Controlled Condensation System consists basically of the following sections: probe; heated quartz filter and filter holder; condenser with medium porosity backup frit; impinger system for collecting SO_2, HCl, and H_2O; and meter box assembly containing pump, dry gas meter, and orifice meter. Figure 4-17 displays the sampling system.

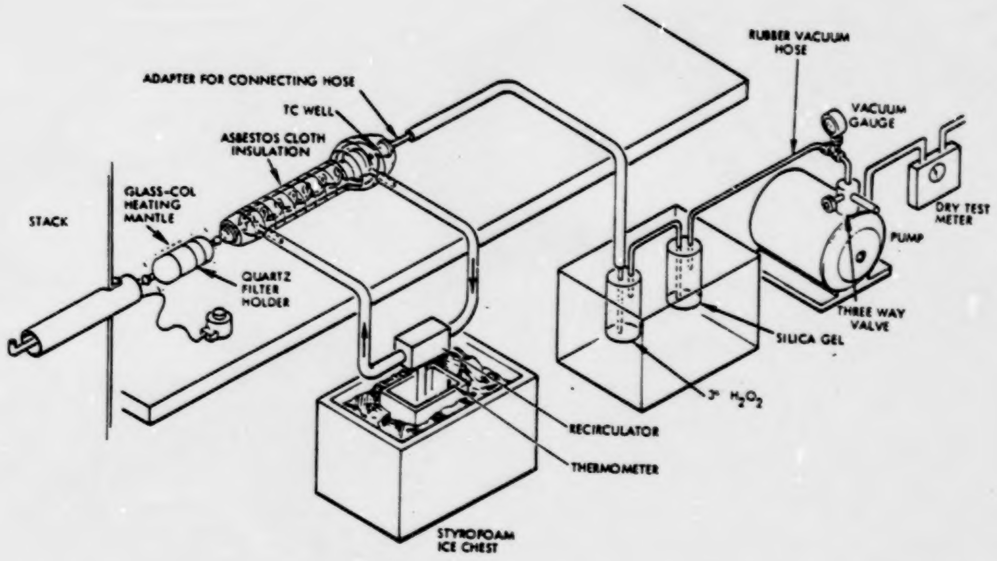


Figure 4-17. IERL Controlled Condensation System

The probe consists of a Vycor (13 mm OD) tube approximately 91 cm long, which is heated to 288°C (550°F) to prevent sulfuric acid condensation. A 6 mm nozzle is attached to the end of the probe, facing away from the flow of the gas stream, to reduce particle collection. Figure 4-18 shows the probe configuration.

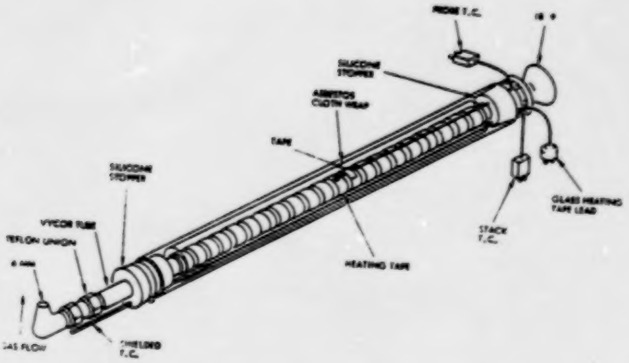


Figure 4-18. IERL Probe Configuration

Normally, when a particle-laden gas steam is sampled with a probe containing a nozzle, the sampling velocity at the nozzle is matched to the velocity of the gas stream. The sample is thus extracted isokinetically. Isokinetic sampling prevents larger or smaller particle from being inertially separated from the gas stream at the nozzle. It is possible that stratification could occur in a duct, thus requiring isokinetic sampling. However, studies[55] have shown that gas stratification in ducts is low (±15%). The probe/nozzle assembly is pointed downstream during the sampling period. Positioning the nozzle in this configuration (Figure 4-18) reduces the quantity of large particles (>3 μ) reaching the filter, thus reducing the SO_2/particle interaction.

Following the probe is an all quartz filter holder which uses a Pallflex tissue-quartz filter to separate the particles from the flue gas. The filter holder is heated with a heating mantle to temperatures sufficient to maintain a gas temperature of >288°C (>550°F) in the filter. The basic construction components of the heated filter are illustrated in Figure 4-19.

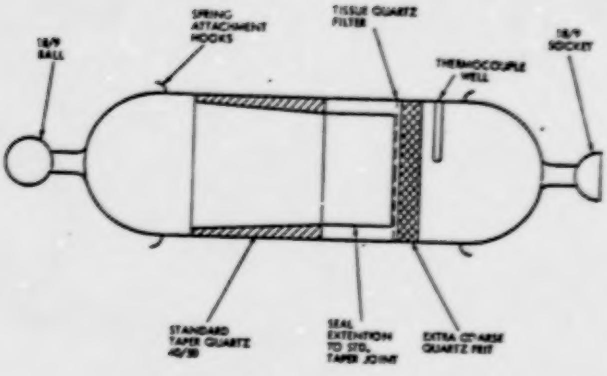


Figure 4-19. IERL High Temperature Filter Holder

Following the particle removal device is a controlled condensation coil. The coil is a Goksoyr/Ross condenser with a back-up medium frit of 10-20 µm pore diameter (Figure 4-20). A water jacket temperature of 60°C (140°F) is maintained around the coil using an immersible heater/recirculator placed in an insulated water bath and connected to the coil with heavy vacuum hose.

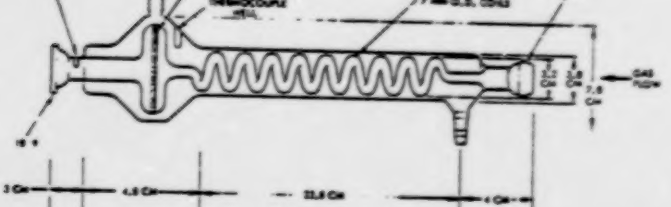


Figure 4-20. IERL Controlled Condensation Condenser

Following the controlled condensation condenser is a series of impingers containing hydrogen peroxide (H_2O_2) to collect SO_2. The normal impinger system contains two H_2O_2 impingers (for SO_2), followed by a Na_2CO_3 impinger for HCl and a silica gel-filled impinger to collect moisture.

The system is operated at a flow rate of 8 lpm for approximately one hour. During this period, fogging of the coil from the condensed sulfuric acid begins. Upon completion of the sampling, the train is disassembled and the condenser is rinsed to collect the condensed sulfuric acid. Analysis for sulfuric acid is performed by titrating the recovered sample with sodium hydroxide (NaOH) to a pH of 4.6 using bromophenol blue indicator. The acid base titration is recommended because of its simplicity and sensitivity.

4.1.6.3 U.S. Environmental Protection Agency (Environmental Science Research Laboratory)

The Environmental Science Research Laboratory (ESRL) of EPA developed a system for measuring primary sulfate emissions that is similar to the IERL controlled condensation system based upon the original work of Goksoyr/ Ross. The system consists of a heated probe and filtering device; a condenser; and a sampling module a containing water bath, pump, and metering device (Figure 4-21).

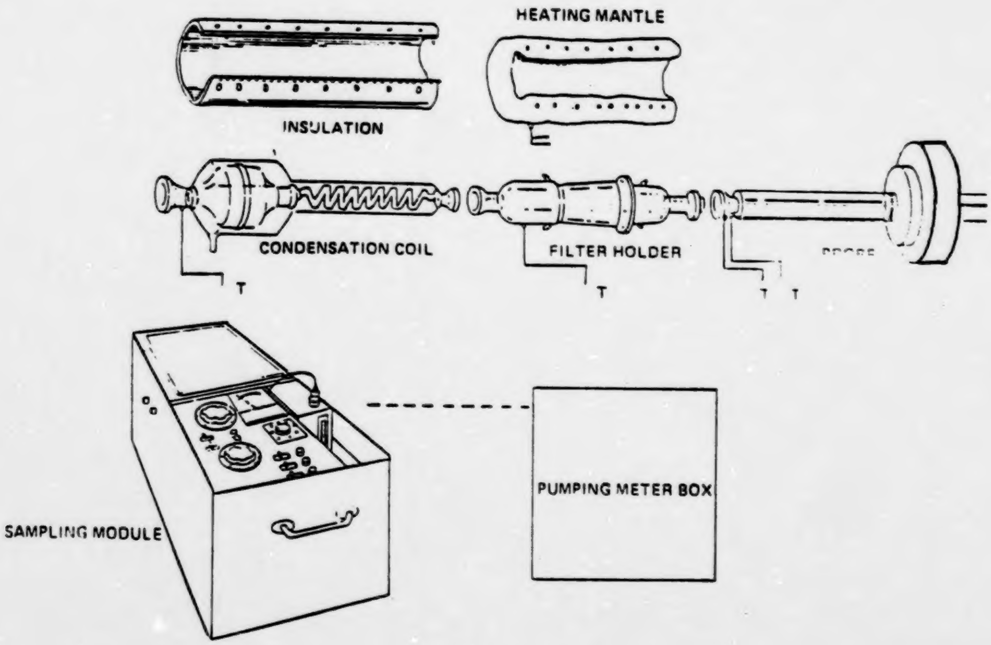


Figure 4-21. ESRL Controlled Condensation System

The sample is extracted from the source through a heated Pyrex® probe which does not employ a nozzle, and through a heated filter where particles are removed from the gas stream. The particle-free gas stream enters the condenser (which is held between 60-90°C), where sulfuric acid condenses. Sulfuric acid that is not retained by the coils is removed by the coarse frit located at the end of the condenser. The gas stream then proceeds to a series of impingers containing hydrogen peroxide for SO_2 absorption.

The analytical technique for detection of condensed sulfuric acid vapor in the coil is the barium-thorin titration, specific for sulfate (SO_4^{-2}); this titration "sees" only the sulfate present in the solution. The IERL system uses an acid-base titration, thus titrating all acids captured.

Since both the IERL and ESRL systems are large and bulky, the more compact miniature acid condensation system (MACS)[56] was developed by ESRL.

4.1.6.3.1 Miniature Acid Condensation System (MACS)

In essence, the MACS system is a combination of a modification of Federal Reference Method 6 and the ESRL controlled condensation system. The coil design of Goksoyr/Ross has been replaced by a temperature controlled glass wool plug. A miniature quartz filter holder is used in the system to remove particulate matter from the gas stream.

The system consists of a heated quartz probe and filter assembly, a glass wool plug maintained at 60°C, and a series of midget impingers for gas determination (Figure 4-22). The stack gas is pulled from the source into a heated quartz filter holder. The filter holder is fitted with a coarse frit, allowing the installation of a 16 mm high-purity quartz filter for particle removal. The filter holder and probe are maintained at 270°C (518°F) to prevent sulfuric acid removal by the filter. The glass plug holder is maintained at 60°C (128°F) for sulfuric acid removal. The plug is composed of a column of pyrex glass wool surrounded by water at 60°C (128°F) from a constant temperature water bath. The sample gas is cooled in the glass plug, allowing sulfuric acid to condense, yet preventing moisture and SO_2 from condensing. After the glass plug, the sample gas is passed through the midget impingers containing hydrogen peroxide absorbing solution where SO_2 is removed from the gas stream. Once again, after sampling, the glass wool plug holder is removed from the sampling train and analyzed for condensed sulfuric acid vapor either by the barium-thorin titration or by ion chromatography.

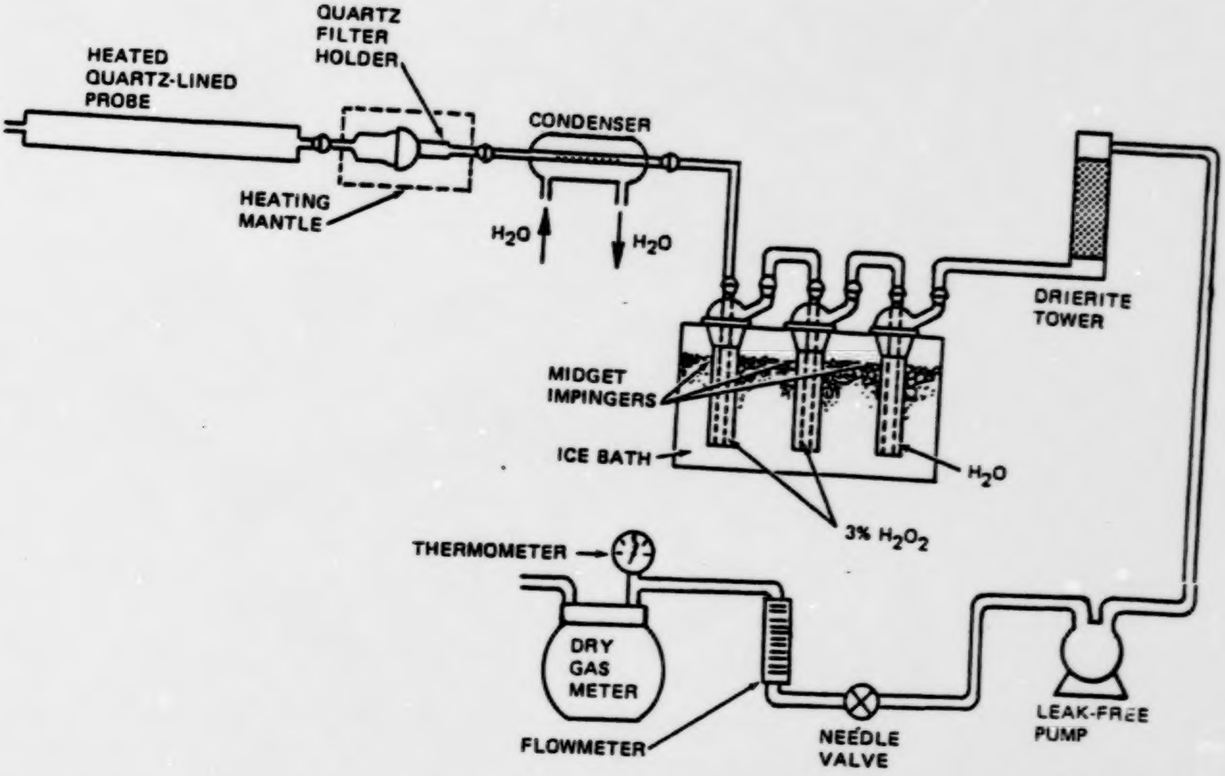


Figure 4-22. Miniature Acid Condensation System

Table 4-4 summarizes the characteristics of each individual controlled condensation system.

TABLE 4-4

CONTROLLED CONDENSATION SYSTEM CHARACTERISTICS

	Brookhaven Controlled Condensation System	U.S. EPA - IERL Controlled Condensation System	U.S. EPA - ESRL Controlled Condensation System	U.S. EPA - ESRL Miniature Acid Condensation System
System Components				
Probe				
o Construction	Pyrex®	Vycor	Quartz	Quartz
o Temperature	200°C	>300°C	>270°C	270°C
Particle Filter				
o Type	Bed	Surface	Surface	Surface
o Size	-	-	-	16mm
o Filter Media	Quartz Plug	Pallflex®	Quartz(ADL)	Quartz (ADL)
o Temperature	Stack	>288°C	270°C	270°C
o Location	In-Stack	After Probe	After Probe	After Probe
o Pretreated	No	No	Yes	Yes
o Frit Type	-	Medium	Coarse	Coarse
o Frit size	-	10-20 μm	-	-
Sulfuric Acid Collection Device	Coil with Back-up Quartz Filter			
o Type		Goksoyr-Ross	Goksoyr-Ross Condenser with Back-up Frit	Glass Tube Packed Quartz
o Size (Length)		34 cm	34 cm	30 mm
o Temperature (water jacket)	60°	60°	65°	65°C
o Frit pore diameter	-	10-20 μm	Medium	-
Sampling Rate	Isokinetically	~8 l/min Constant Flow Rate	~10 l/min Constant Flow Rate	~3 l/min Constant Flow Rate
Analytical Techniques				
o Sulfuric Acid Determination	Acid/Base	Acid/Base	barium-thorin	barium-thorin or Ion Chromatography
o Auxiliary Determination	SO_3/SO_2	SO_2, HCl, H_2O	SO_3/SO_2	
Cost (Approximately)	$6500.00	$8250.00	$8250.00	$7663.30

4.2 Automated Techniques

Concurrent with the research development and experimentation of manual extractive systems, several automated systems were also being developed and tested in the U.S. and England. This section deals with the automated approach to monitoring sulfuric acid vapor from gas streams by means of three basic systems:

- U.S. EPA Sulfuric Acid Mist Monitor (SAMM)
- Severn Science LTD SO_3 Monitor (SSL)
- Laser Analytics Tunable Diode Laser (TDL)

4.2.1 U.S. EPA - ESRL Automated Sulfuric Acid Mist Monitor (SAMM)

One of the first automated applications of the controlled condensation condenser was the Sulfuric Acid Mist Monitor (SAMM).[57] The automated sulfuric acid mist monitor consists of three major components: (1) a probe and particle removal device; (2) a condensation coil with conductivity measuring cell, and (3) assorted metering devices and pumps. The complete monitoring system is housed in a 91 X 76 X 31 cm enclosure and weighs approximately 41 kg (see Figure 4-23).

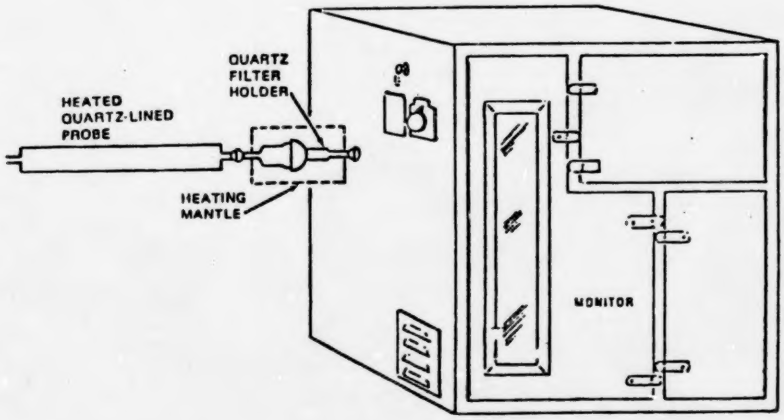
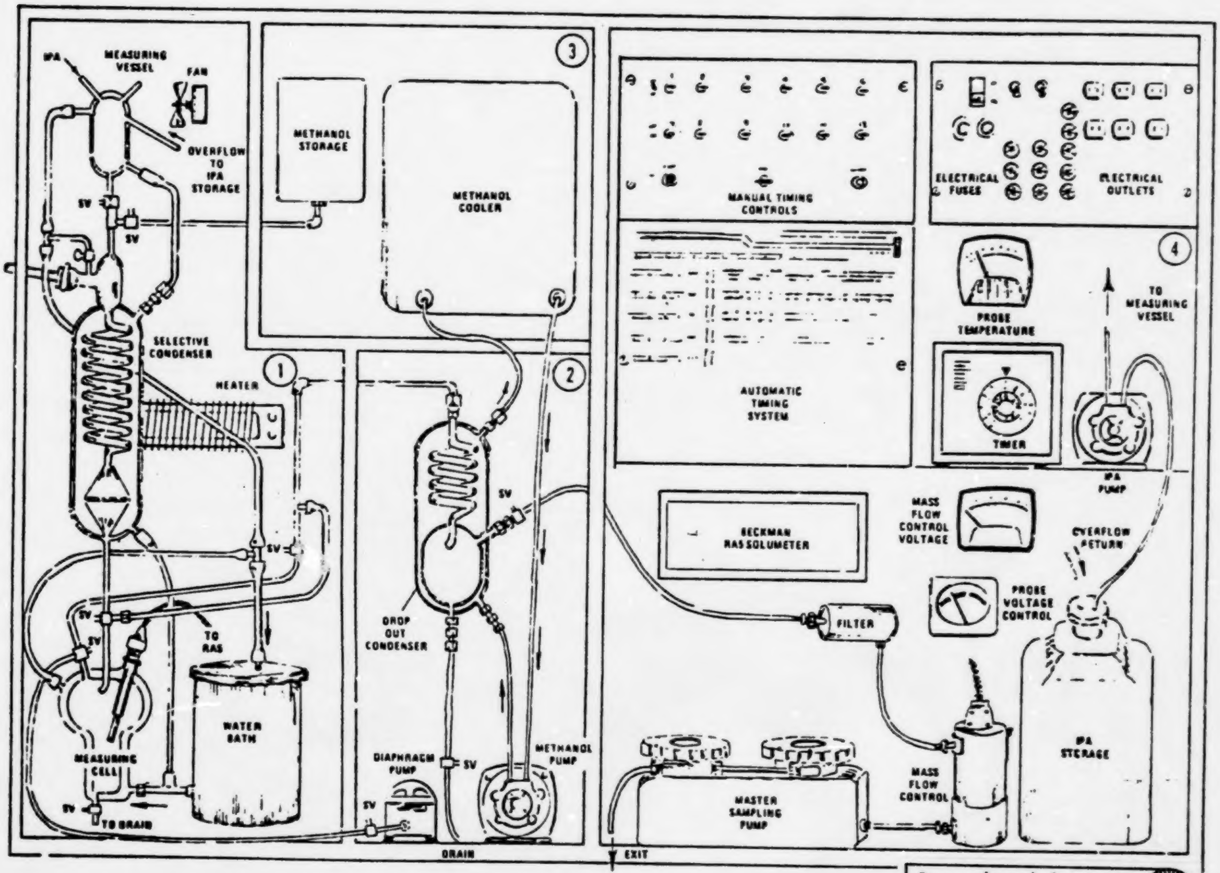


Figure 4-23. ESRL Sulfuric Acid Mist Monitor

The SAMM system condenses sulfuric acid from the gas stream by means of a water-cooled condenser that is maintained below the acid dew point but above the water dew point. After a sufficient period of time, the coil is rinsed with a measured amount of water/isopropanol solution into a conductivity cell which measures the conductivity of the sulfuric acid-water solution. Once measured, the solution is pumped out of the conductivity cell and exhausted to a waste receiving jar. The system is automated by a master control that operates the various components of the sampling system. The system enclosure consists of four major compartments, as shown in Figure 4-24.



Reproduced from best available copy.

Figure 4-24. Sulfuric Acid Mist Monitor Enclosure

Compartment 1 contains the measuring vessel, the Goksoyr-Ross condenser, the measuring cavity, and the water bath. The sample enters at the top of the water cooled condenser (Figure 4-25). As the gas stream spirals through the condenser, the sulfuric acid condenses on the inside surfaces of the coil. A backup quartz frit positioned at the end of the coil traps any acid droplets that might not have been condensed in the coil. Once a sufficient amount of acid has been collected by the coil, a predetermined amount of isopropanol is rinsed through the coil and quartz wool plug into the measuring cell. The conductivity meter located in the measuring cell measures the conductivity of the solution.

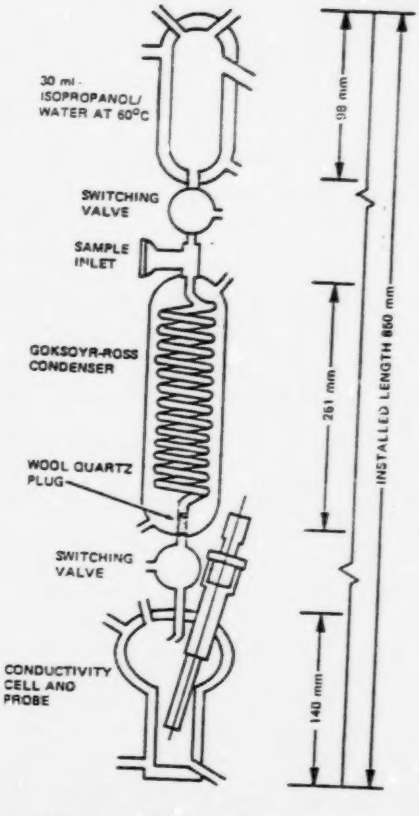


Figure 4-25. SAMM: Compartment #1

Once the conductivity has been measured, the sample is pumped out of compartment 1 and into compartment 2 where a dropout condenser serves to collect the water/isopropanol rinse and vapors to protect the mass flow control and assorted sampling pumps. Compartment 3 contains the methanol refrigerant unit that chills the 50% aqueous methanol solution used in the dropout condenser.

Finally, compartment 4 contains the sampling controls and timing system that enable the system to extract, analyze, and eject each individual sample automatically . The cycling time can be varied from 1 to 999 seconds, depending upon the sulfuric acid concentration in the flue gas. The sampling rate can be controlled by adjusting a variable pot located in the back of the monitor. By adjusting the pot voltage (0 to 5 volts), a flow rate between 0 and 20 l/min can be obtained.

Calibration of the monitor is performed by injecting known amounts of sulfuric acid into the condenser inlet just before the isopropanol wash cycle. The calibration can be performed with three different water-isopropanol solutions. However, due to the high dielectric constant of water, the collection of source samples is usually performed with a 90-95% aqeuous solution of isopropanol. Figure 4-26 shows a series of sample calibration curves for the monitoring system.

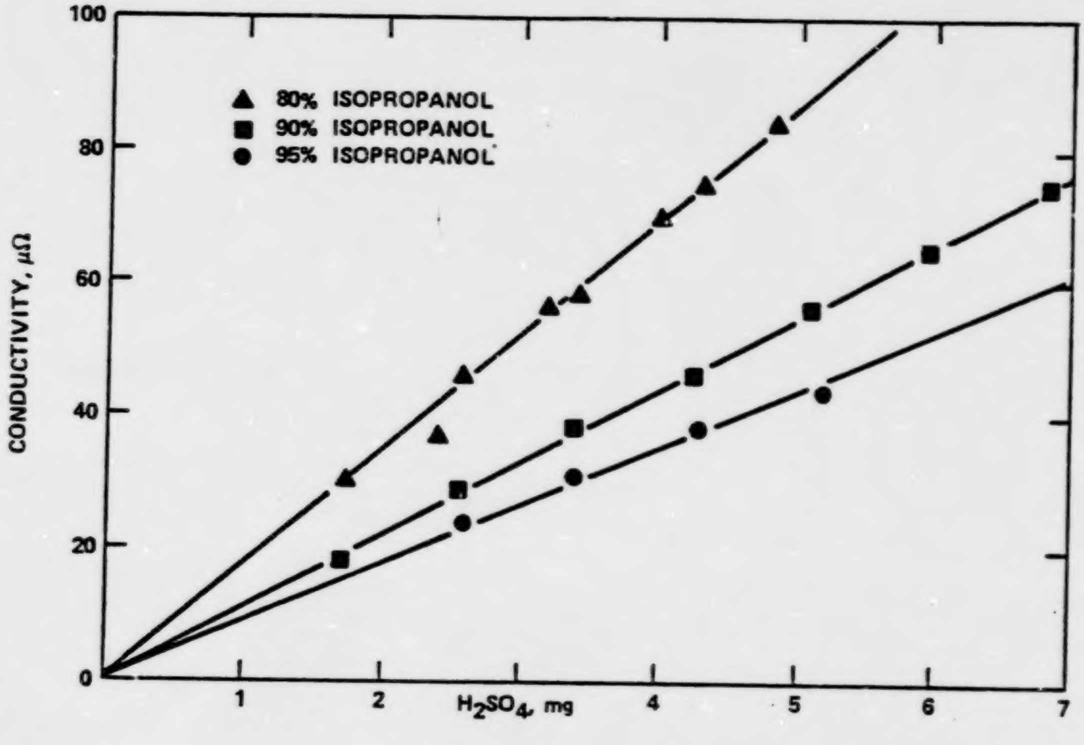


Figure 4-26. SAMM Calibration Curves

As with other sampling techniques, the separation of particulate sulfate and sulfuric acid is important. Initially, the monitor contained a heated cyclone[58] to dropout the large particles before the gas stream entered the condenser (Figure 4-27).

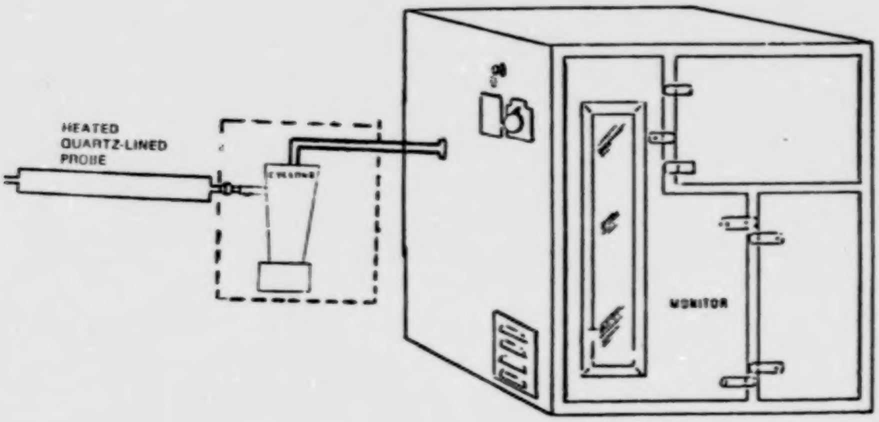


Figure 4-27. SAMM with Heated Cyclone

Recent modifications to the unit now employ a heated quartz filter holder (similiar to the controlled condensation system) to trap and remove particulate matter down to 0.2 microns from the sample gas stream.

Since the determination of sulfuric acid concentration requires an accurate measurement of the sampled gas volume, a calibrated orifice meter is located in compartment 4 of the monitor. The meter on the all-stainless steel orifice monitors total gas flow in ACFM by measuring the differential pressure across the orifice.

Concurrent with the above developments, Severn Science Ltd. of England, through the Central Electric Generation Board, also developed an automated sulfuric acid mist monitor.

4.2.2 Severn Science Limited SO_3 Monitor

The Severn Science Limited[59] SO_3 monitor consists of four basic units: a probe unit to sample the flue gas, an umbilical cord to transfer solution from probe to analyzer, an analyzer unit to detect sulfate ions, and a recorder (Figure 4-28).

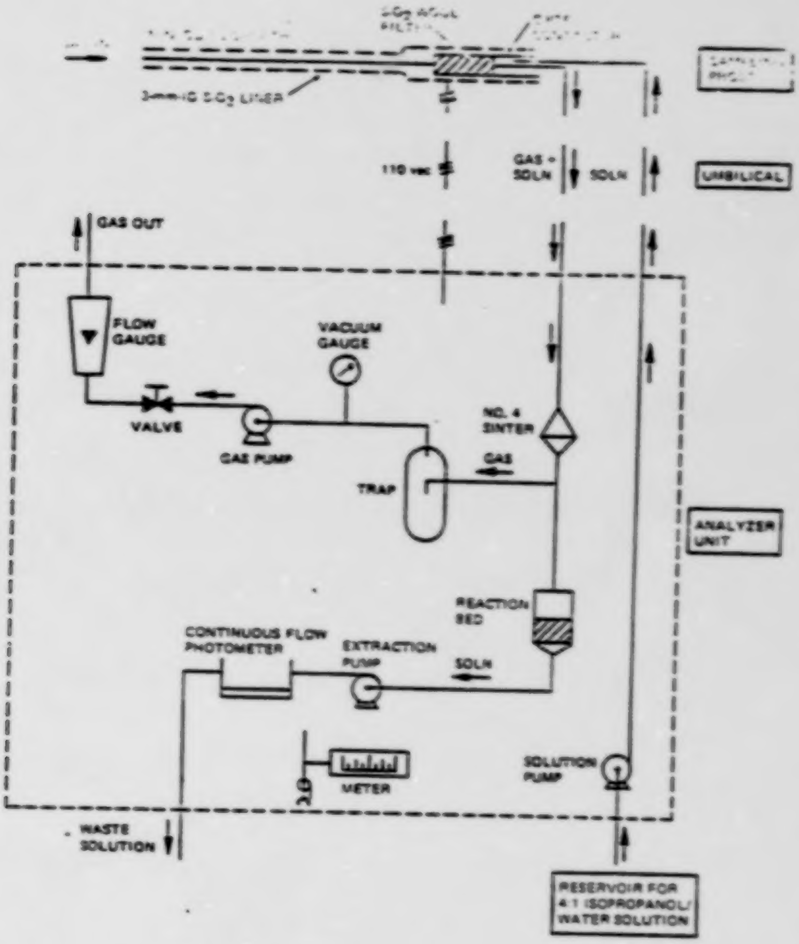


Figure 4-28. Severn Science Limited SO_3 Monitor

The probe unit consists of a heated quartz tube, a SiO_2 wool filter, and a graphite-filled PTFE gas/liquid contactor. The flue gas sample is removed at a rate of 0.5 liters/minute by a pump located inside the analyzer unit. The gas then moves through the heated silica glass wool plug to remove particles. The probe and filter are heated so sulfuric acid does not condense until it reaches the 80% isopropanol solution. Next, the gas/liquid contactor enables the oxidation of SO_3 by 80% isopropanol sprayed into the gas stream. Hence, SO_3 and H_2SO_4 are retained with minimal interference from SO_2. Once the contact with 80% isopropanol is made, the solution/gas mixture is transferred to the analyzer via the umbilical cord for detection.

In the analyzer, the gas is separated from the acid solution and is pumped to the atmosphere. The sulfuric acid solution is then analyzed by passing it through a capsule of barium chloranilate crystals. These crystals react completely with the acid to form a purple solution of acid chloranilate ions, as per the following reaction:

$$H_2SO_4 + BaC_6O_4Cl_2 \longrightarrow BaSO_4 + H_2C_6O_4Cl_2$$

The colored acid chloranilate solution is pumped to a flow-through colorimeter, where its absorbance at 535 nm is measured.

The monitor is calibrated by injecting known concentrations of sulfuric acid at the probe inlet and recording absorbance. A calibration curve is developed from this information.

Table 4-5 summarizes the characteristics of the continuous sulfuric acid monitors described above.

TABLE 4-5

CONTINUOUS SULFURIC ACID MONITOR CHARACTERISTICS

	Severn Science Limited Continuous SO_3/H_2SO_4 Monitor	Dew Point Meter	Sulfuric Acid Mist Monitor (SAMM)
System Component			
Probe			
o Construction	Silica Glass	Stainless Steel	Pyrex Glass
o Temperature	250°C	Glass Tip Variable	250°C
Particulate Filter			
o Type	Bed	-	Surface ESP
o Size		-	-
o Filter Medium	Silica Wool	-	-
o Temperature	200°C	-	-
o Location	Out-of-Stack	-	-
o Pretreated	No	-	-
o Frit Size	-	-	-
Sulfuric Acid Collection			
o Device	Absorption	Conduction	Condensation
o Solution	80% IPA	-	-
o Mechanism	-	Glass	-
Sampling Rate	0.5 1/min	-	Variable
Analytical Technique			
o Sulfuric Acid	Spectrophotometrically	Current Indicator	Conductivity
Cost (Approximately)	$17,000	$5,000.00	$12,000

4.3 Remote Monitoring

Conventional methods for extracting and analyzing for sulfuric acid vapor from combustion sources usually involve some form of wet chemical interaction between the pollutant and the collection media. Historically, to ensure maximum collection efficiency, prior knowledge of interfering species is required.

Recently, spectroscopic techniques have been developed which offer the potential of performing the analysis of sulfuric acid vapor without sample extraction, thus minimizing interfering species. Utilizing the response characteristics of sulfuric acid vapor in the infrared portion of the electrostatic spectrum, these techniques enable quantitative identification and analysis in the presence of these interfering species. Recent work in this research area is described in the following sections.

4.3.1 Remote Optical Sensing of Emissions (ROSE)

The EPA Remote Optical Sensing of Emissions (ROSE)[60] system consists of a commercially available Fourier Transform Infrared Interferometer (FT-IR) System mounted in a van. To support the FT-IR system, other auxiliary items including a weather station for meteorological data, a laser range finder for measuring path lengths, a 10 kw generator for maintaining a stable electrical environment, and a software package for interpreting absorption and emission spectra are also located in the van. A schematic of the layout of the component parts is shown in Figure 4-29.

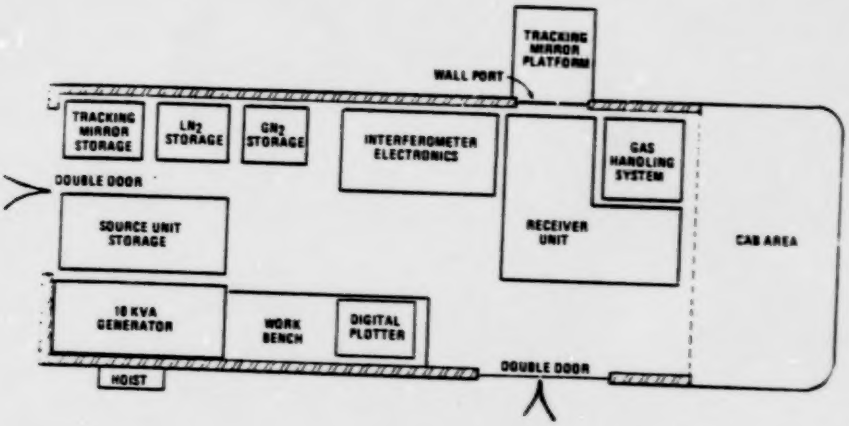


Figure 4-29. ROSE System: Van Configuration

The FT-IR system can operate either in the absorption (active) mode or the emission (passive) mode, as demonstrated in Figure 4-30.

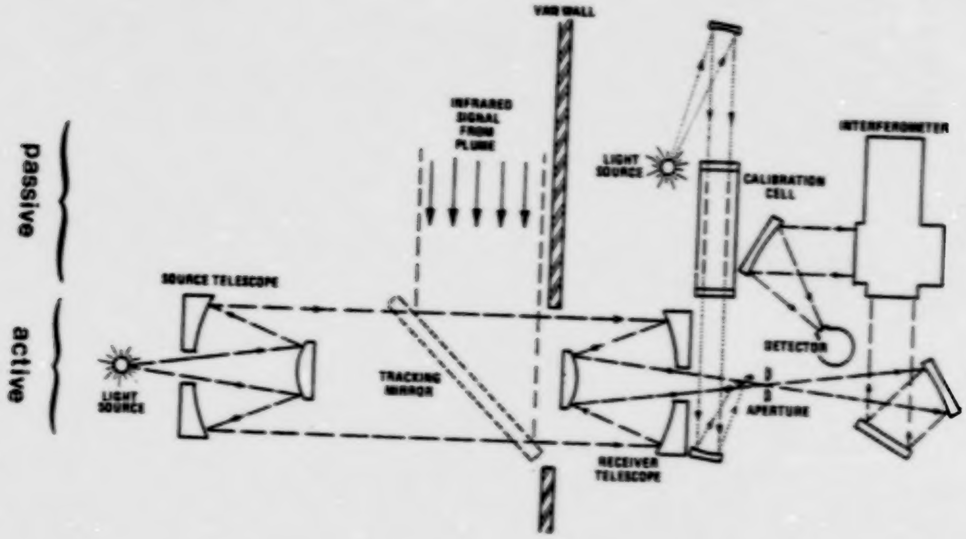


Figure 4-30. ROSE System: Optical System

In the active mode, a light source-telescope is positioned remotely from the van for long path absorption measurements. The light source is a 1000 W quartz-halogen lamp positioned behind a focusing telescope used to project the IR energy across the monitoring source to the receiving telescope, as shown in Figure 4-30 and Figure 4-31.

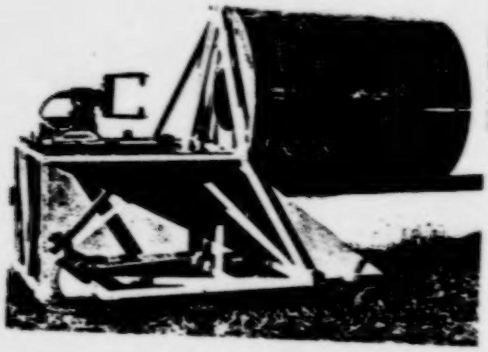


Figure 4-31. ROSE System: Light Source-Telescope

If sulfuric acid vapor is present in the light path, then it will absorb IR energy at characteristic wavelengths. By monitoring the amount of energy absorbed by the pollutant between the light source and the receiving telescope and comparing that absorption to a known concentration contained in a reference cell, a concentration value for the pollutant can be calculated from Beer's Law:

$$T = \exp[-K(\nu,T)\,CL] = \text{transmittance at frequency} \quad (\text{cm}^{-1}),$$

where :

$K(\nu,T)$ = spectral absorption coefficient,
C = gas concentration (ppm or molecules/cm^3),
L = pathlength (meters), and
T = gas temperature (degrees Kelvin).

In the calibration measurement, C and L are known and K is determined. In the field measurement, K and L are known and C is calculated. To assist in the calculations, a software program provided for the on-board computer compares the field spectrum with a calibration spectrum and calculates the unknown concentration.

The receiver telescope collects the remaining energy from the remote light source that is not absorbed by sulfuric acid vapor and focuses this energy at the entrance aperture of the interferometer. Once in the interferometer, the incoming IR energy is divided by a beam splitter into two equal components, as depicted in Figure 4-32.

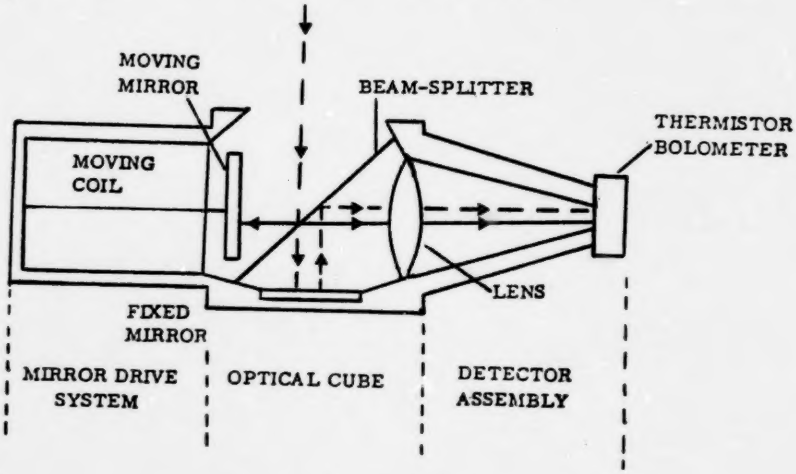
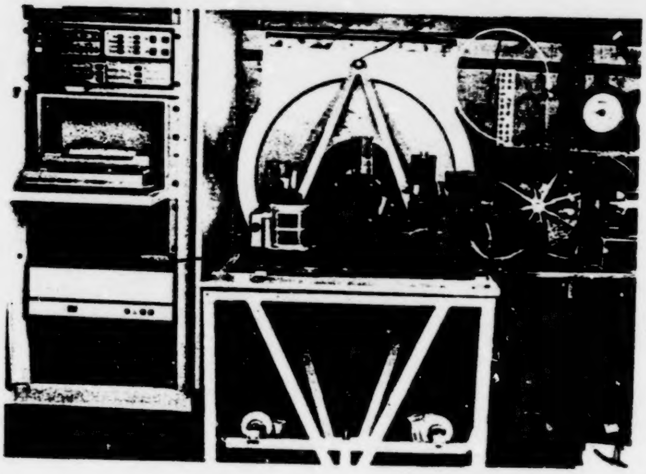


Figure 4-32. ROSE Interferometer

Half of the energy is allowed to pass through the beam splitter to a fixed mirror, where it is reflected back to the beam splitter and focused onto the detector. At the same instant, the other half of the IR energy is focused upon a moving mirror by the beam splitter. A phase difference is introduced by the moving mirror, and the output signal I(x), given as a function of mirror movement (x), is called the interferogram. The interferogram is the Fourier transform of the spectrum produced by the FT-IR. This spectrum is reconstructed and interpreted by taking the inverse transform through a digital computer.

The detector used to sense the IR energy is a dual-element sandwich type configuration. For the spectral region 1800 to 6000 cm^{-1}, an InSb detector is used. For the longer wavelength region, 600 to 1800 cm^{-1}, HgClTe detector is used. Each of these IR regions can be scanned separately or at the same time, depending upon the mode of operation. The detecor senses the IR energy as received from the interferometer. Consequently, the ROSE system is a real time monitor. Figure 4-33 displays the receiver telescope, interferometer, and detectors of the ROSE system.



Reproduced from
best available copy.

Figure 4-33. ROSE System: Electronics Receiver Telescope and Interferometer

In the emission (passive) mode, IR energy from a source is aligned to the entrance of the interferometer by means of a tracking mirror. The tracking mirror is mounted to the side of the van, as shown in Figure 4-34.

Figure 4-34. ROSE System: Tracking Mirror

Once the IR energy is focused properly, it follows the same analysis/detection scheme as when the system is in the absorption (active) mode.

Emission spectra are calibrated in terms of spectral radiance by comparison with the spectrum of a black body source at known temperature. Once again, calculations are carried out by the on-board software system.

An example of a typical spectrum obtained with the ROSE system is shown in Figure 4-35. The left side of the figure represents sulfuric acid emissions from a brick kiln, while the right side is the spectrum of a standard gas cell of sulfuric acid.

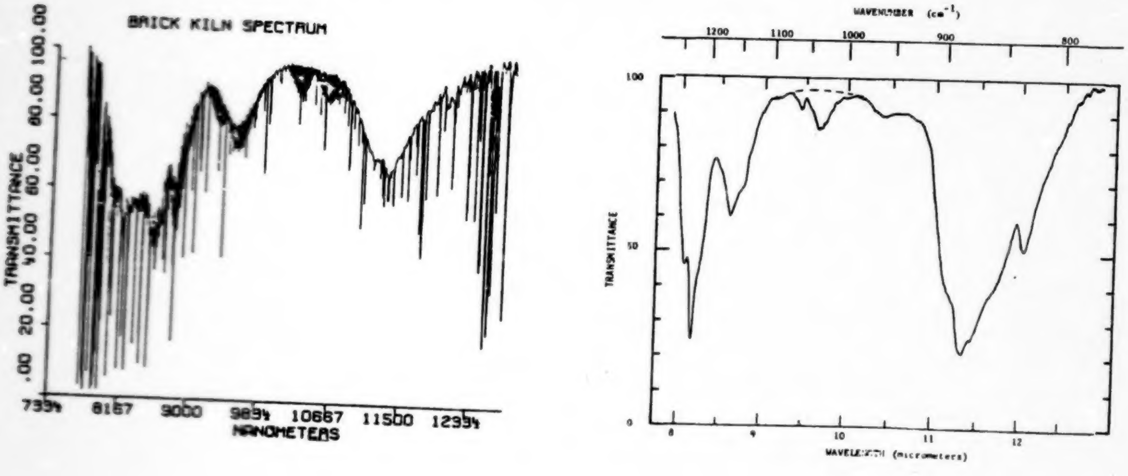


Figure 4-35. ROSE System: Typical IR Spectrum of Sulfuric Acid Vapor

4.3.2 Tunable Diode Laser

Another technique that employs real-time monitoring is the Tunable Diode Laser[61] (TDL) technique developed by Laser Analytics for the Environmental Protection Agency. Monitoring a compound by spectroscopic techniques requires that its absorption be well characterized in the spectral region of interest. Although spectroscopic measurements of species such as SO_2, NO, CO, and CO_2 are routine in the infrared, sulfuric acid presents a far more difficult problem. This molecule displays no sharp absorption features in the infrared and is not amenable to detection systems based upon gas filter correlation. Laser Analytics' solution to this measurement problem is a dual wavelength Tunable Diode Laser (TDL) system capable of selecting wavelengths of interest apart from those of interfering species.

The TDL system is a double pass in-situ monitor that measures differential absorption in the infrared. Two tunable diode lasers are locked to two specific frequencies, providing analytical and background absorption information. The difference in absorption between the analytical and background wavelength is directly proportional to the sulfuric acid concentration. Although sulfuric acid shows broad band absorption, the TDL system is capable of selecting narrow IR regions of the electromagnetic spectrum due to its high resolution capability. Figure 4-36 demonstrates the high resolution capability of the Tunable Diode Laser (TDL) system as compared to the Fourier Transform Infrared (FT-IR) system.

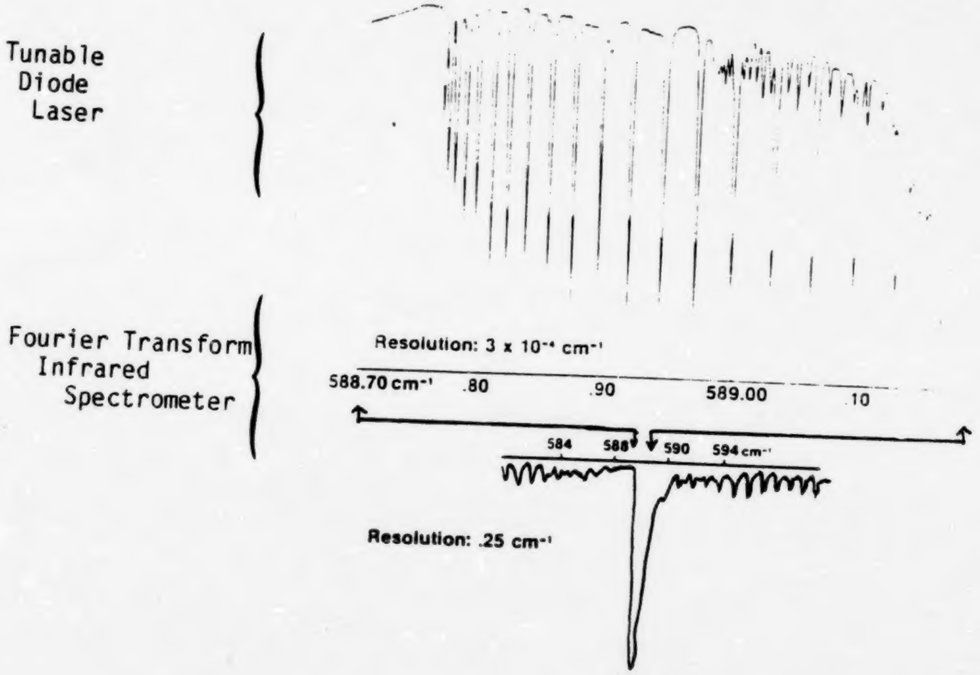
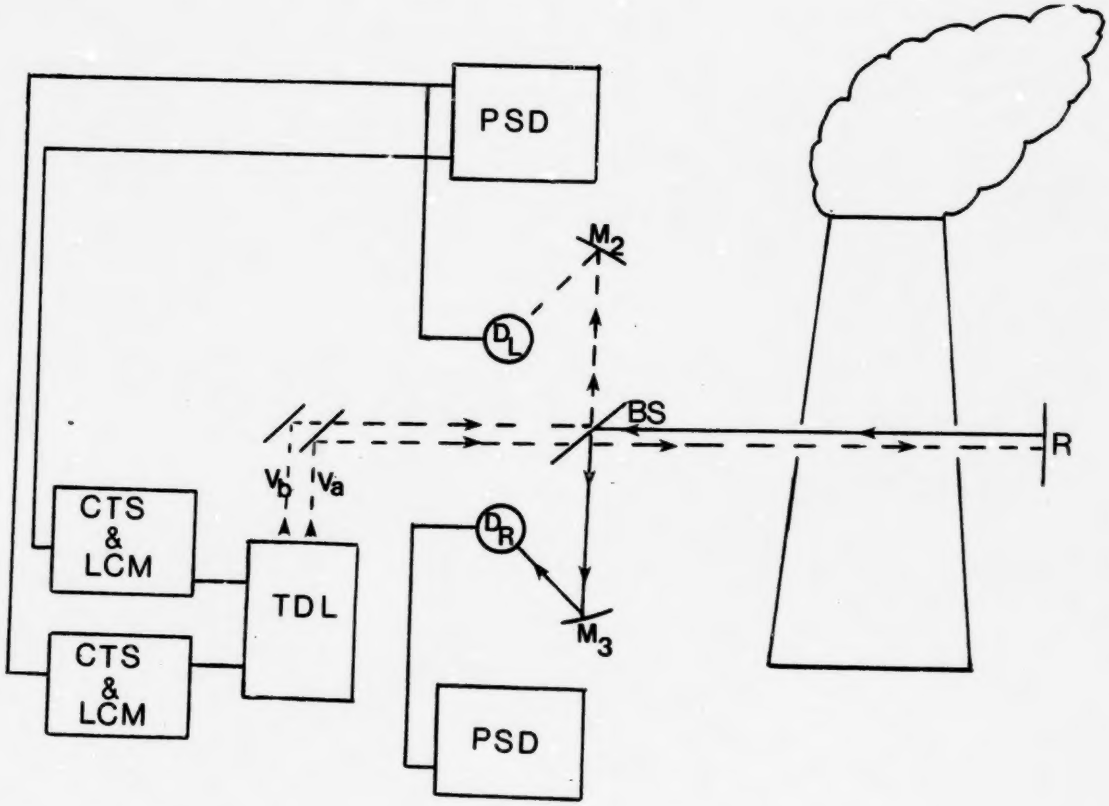


Figure 4-36. Comparison Spectra: TDL and FT-IR

The principle of dual wavelength differential absorption is further illustrated in Figure 4-37.



[Where: CTS = Cryogenic Temperature Stabilizer, LCM - Laser Control Module, TDL = Tunable Diode Laser, PSD = Phase Sensing Detector, D_L = Detector for Pollutant, D_R = Detector for Reference, BS = Beam Splitter, R = Retroflector.]

Figure 4-37. Tunable Diode Laser Monitoring of Sulfuric Acid

Two frequencies of infrared energy are generated: one frequency (V_a) lies within the IR spectrum where sulfuric acid vapor absorbs and a second frequency (V_b) lies outside that region. These frequencies are generated by the two Tunable Diode Lasers (TDLs) mentioned earlier. The combined outputs of the lasers at infrared frequencies V_a and V_b are divided by a beam split on BS. The fraction of the infrared radiation directed to detector D_L via mirror M_2 establishes the background infrared frequency (V_b). The transmitted infrared frequency (V_a) passes across the stack to a retroreflector (R) and returns to the electronics package. This frequency is attenuated in proportion to the sulfuric acid content of the stack gas, according to the Beer-Lambert Law:

$$T = I/I_0 = \exp(- \alpha CL)$$

Where:

T = transmittance of light through the flue gas,
I_0 = background intensity of light (V_b) entering the gas,
I = pollutant intensity of light (V_a) leaving the gas,
α = absorption coefficient,
C = concentration of the pollutant, and
L = path length (meters).

Laser signal intensities are related to measured intensities by the relationship:

$$I_0 = KI,$$

where the K includes beam splitter and other optical efficiencies as shown in the Beer-Lambert Law.

Once the transmitted frequency re-enters the electronics package, beam splitter BS once again directs this energy to detector D_R via mirror M_3. This signal is measured and compared to the background frequency (V_b) measured by detector D_L. Consequently, the detection of sulfuric acid vapor on a real time basis is determined through the principle of dual wavelength differential absorption.

5.0 SULFURIC ACID MONITORING SYSTEMS
DISCUSSION AND EVALUATION

The ability to accurately monitor sulfuric acid vapor is greatly dependent upon the sensitivity of the analytical system used to distinguish between this vapor and other pollutants. The sampling system may utilize either in-situ, extractive, or remote techniques, but it must be free of (or at least capable of accounting for) interferences from such common species as:

- Water (vapor or droplet)
- Particulate matter
- Variable oxygen content
- Temperature
- Varying sulfuric acid concentration

The following discussion focuses on these and other variables that affect the collection of sulfuric acid by the analytical technicques presented in Section 4.0.

5.1 Manual Techniques

5.1.1 Theoretical Dew Point

Most sulfur in power plant flue gases appears as SO_2, with typical SO_3 levels ranging from 1.0% to 5.0% of the SO_2 value. The production of sulfur oxides in the flue gas can be expressed by the following equation:

$$H_2O_{(g)} + SO_{2(g)} + 0.5O_{2(g)} \longrightarrow SO_{3(g)} + H_2O \longrightarrow H_2SO_4$$

Thermodynamic analysis of the above equilibrium, by calculating H_2SO_4, H_2O, and SO_3 partial pressures from enthalpy, entropy, free energy, and heat capacity values, provides a theoretical basis for predicting acid dew point and condensate composition.[62]

The basic problem in relating the sulfuric acid concentration to the dew point is the effect of water. For a given sulfuric acid concentration, the dew point will change appreciably as the moisture level changes.

Therefore, relating acid concentrations of a flue gas to its acid dew point involves concurrent moisture level determination. Variation of dew point with sulfuric acid vapor content of gases having different water vapor concentrations is shown in Figure 5-1, where a range of 5% to 15% water vapor corresponds to a dew point range of ~126°C (260°F) to ~141°C (287°F) for a 10 ppm sulfuric acid vapor concentration.

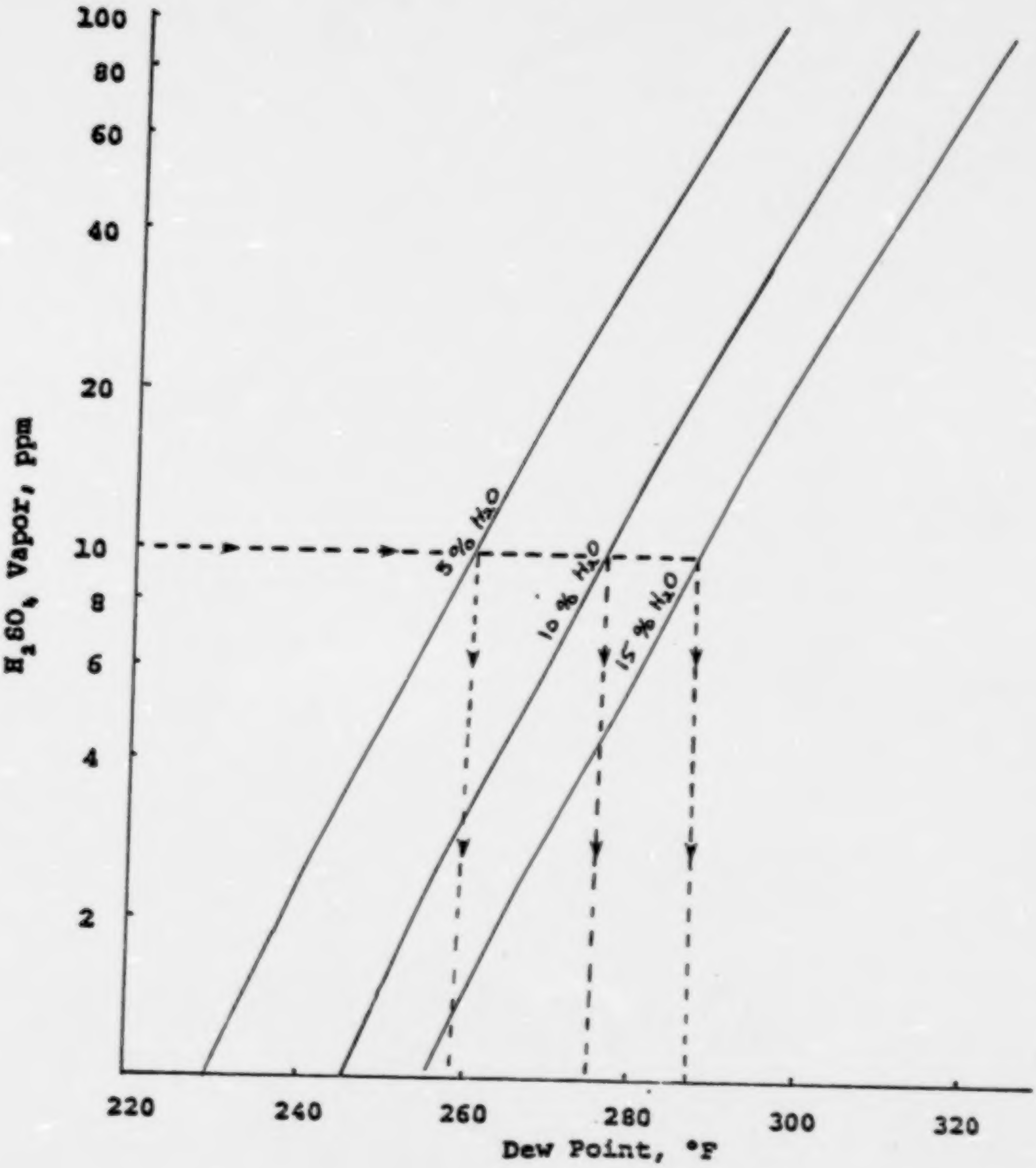


Figure 5-1. Variation of Dew Point with Varying Water Vapor Concentration

Johnstone was the first to relate dew point of flue gases to the amount of sulfuric acid in the gas stream. Later, Abel[63] and Greenewalt[64], Gmitro[65], Lisle[66], Muller[67], and Taylor[68] all developed dew point curves based on calculated partial pressures. Figure 5-2 compares the results of the various investigators. However, to make an exact comparison, all curves should be of a gas of the same % H_2O vapor.

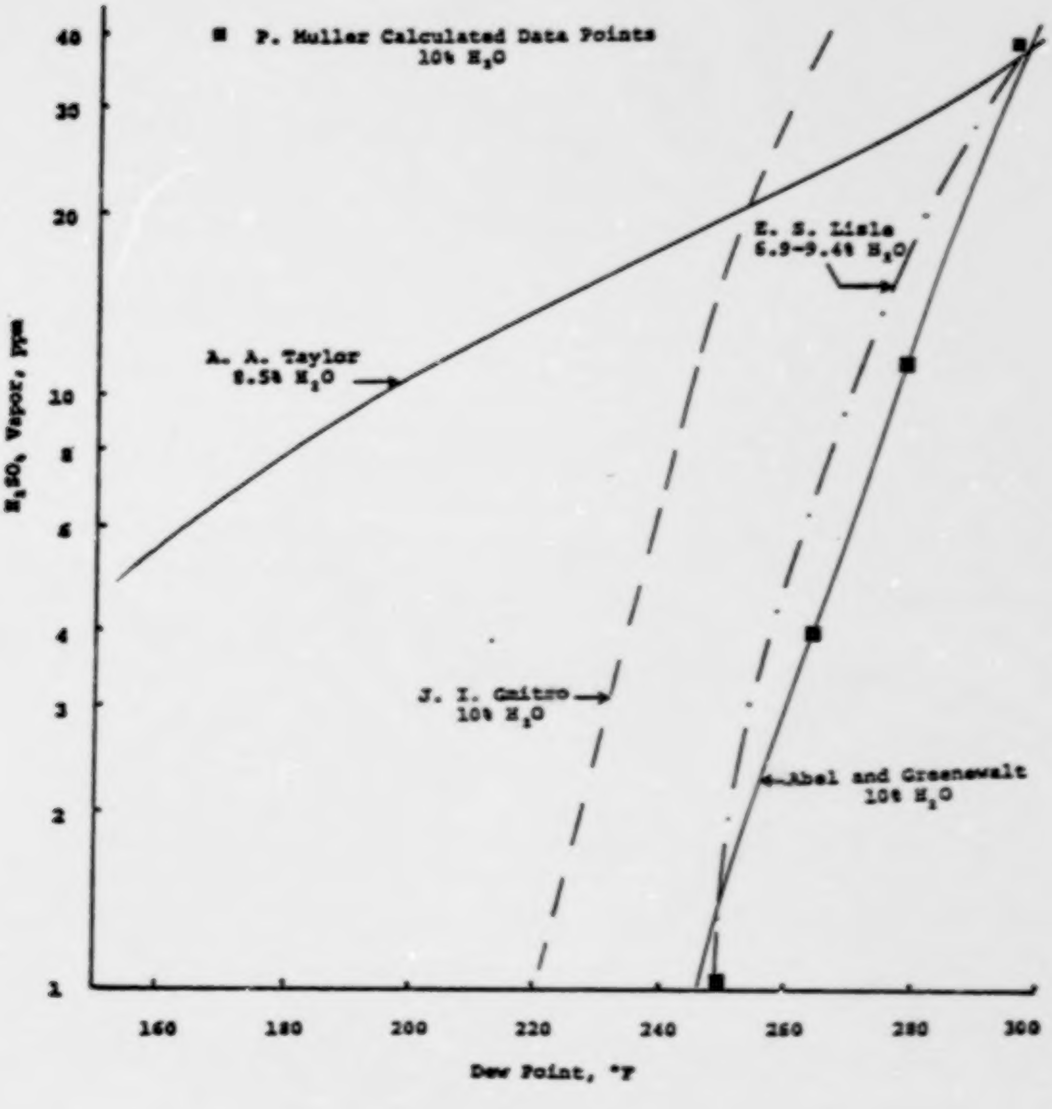


Figure 5-2. Theoretical Dew Points Curves Based on Partial Pressure Calibration of Sulfuric Acid Vapor.

As with most combustion processes, the varying load of the boiler changes the chemical composition of the gas stream and also changes the moisture level. This variation leads to error in determining the theoretical dew point of a flue gas stream.

5.1.2 Deposition Rate Probe

As discussed earlier, deposition rate probes are constant temperature probes enabling culturic acid to deposit by controlling probe temperature at or below the expected dew point. Although early techniques for monitoring sulfuric acid in flue gas streams employed the deposition rate probe, it is now limited in its application. The major interference with the disposition rate probe is other acids may have a dew point at or below sulfuric acid, consequently, hey will also be determined as sulfuric acid. The technique lacks specificity, sensitivity and accuracy.

In some tests, it is necessary to adjust the deposition rate results and the dew point determined to new values because of the length of time it takes the probe to rise from ambient temperature to the desired temperature.[69] As the probe is heated, it initially passes through the dew point, collecting acid before it reaches the desired temperature. Also, a limited number of data points of acid deposition rate versus temperature graph can be obtained at any one time, further limiting the accuracy of the method.

5.1.3 Dew Point Meter

The dew point meter measures the conductivity of condensed acid between two electrodes embedded in a probe surface that is cooled to a temperature at or below the acid dew point of the flue gas stream. This approach was first used in England as a means of monitoring corrosion potential of a flue gas stream.

The dew point meter functions on the principle of concurrent moisture determination. As the moisture in the flue gas changes, so does the dew point. However, the dew point meter measures only the gas phase sulfuric acid, not acid condensed into liquid droplets or adsorbed on solid particles. Consequently, the results obtained from the dew point meter can be affected by a heavily dust-laden gas stream.[70] In order to maintain a steady state current, indicating an equilibrium between rate of evaporation and condensation of sulfuric acid, the probe tip must be free of particulate interference. When particulate adheres to the probe surface, erratic current flow occurs, leading to poor repeatability and making interpretation impossible. Therefore, accurate determination of the dew point of a gas stream is best achieved by avoiding particulate buildup on the probe surface.

Additionally, gas streams containing <5 ppm SO_3 and a very low moisture concentration (<4%) can give incorrect readings on the dew point meter.[71] An adequate layer of sulfuric acid is not maintained on the probe tip at these concentrations, and the resulting current flow is, again, erratic.

5.1.4 Federal Reference Method 8

Originally intended for sulfuric acid plants as covered under New Source Performance Standards, Federal Reference Method 8 has recently been applied to other combustion sources not associated with the production of sulfuric acid. This, in part, is due to the recent interest in sulfur emissions and their adverse effects on the public health.[72-77] Recent studies have shown a correlation between crude oil usage and total suspended particulate in the Northeast[78] and a high conversion rate (5% to 10%) of SO_2 to SO_4 in the flue gas stream of fossil fuel-fired steam generators (FFFSG).[79] Consequently, a renewed interest in measurement technology for monitoring total sulfates and unassociated gaseous sulfuric acid emissions has occurred.

However, this recent application of Federal Reference Method 8 to other than sulfuric acid plants has led to erroneous reporting of emission factors associated with tested sources. Early users of the method for testing other processes failed to consider the differences between process streams. Emissions from sulfuric acid plants are usually low in particulate loading and moisture, whereas characteristic emissions from FFFSG are high in both particulate and moisture loading. This difference leads to potential sampling problems with Federal Reference Method 8; the method cannot distinguish between unassociated gaseous sulfuric acid and related particulate sulfate. This is due to the lack of a prefilter to exclude particulate matter from the 80% isopropanol impinger. Once in the impinger, the particulate matter can contribute to the total gaseous sulfuric acid measurements as a sulfate salt by catalyzing the oxidation of SO_2 to sulfate, in the liquid phase, through action of trace metals. In addition, the absorption and oxidation of SO_2 in the isopropanol impinger has been a major concern to users of the Reference Method.

To determine the accuracy of Federal Reference Method 8 and to examine potential interferences, the U.S. Environmental Protection Agency conducted a collaborative test study at a sulfuric acid plant. Six laboratories simultaneously sampled the same stack, using two Method 8 sampling trains per laboratory. The collaborative test determined that repeatability (within-laboratory precision) of the method was 7.19 mg H_2SO_4/m^3 and 22.30 mg SO_2/m^3 and that reproducibility[80] (between laboratory precision) of the method was 8.03 mg H_2SO_4/m^3 and 31.10 mg SO_2/m^3. The collaborative test also demonstrated a detection limit of 9.05 mg SO_3/m^3.

In addition to the collaborative test, EPA conducted and sponsored several studies to determine proper operational parameters of the Federal Reference Method 8 sampling train, including (1) SO_2 retention in the IPA impingers, and (2) collection efficiency of the Greenburg-Smith impinger for sulfuric acid mist.

In determining the retention of SO_2 by the IPA impinger, EPA conducted a series of tests[81] using a source simulator facility capable of maintaining a constant and controllable source of SO_2, O_2, CO_2 and H_2O. The test involved operating the source simulator at two different levels of SO_2 (500 and 1000 ppm) while sampling by Federal Reference Method 8. Table 5-1 indicates the results of those tests.

TABLE 5-1

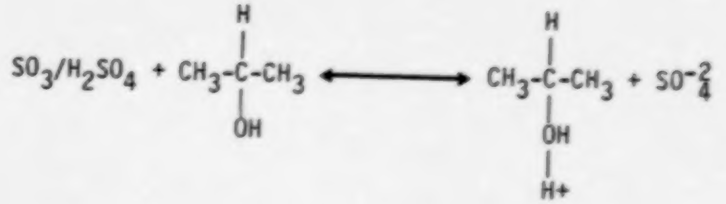
RETENTION OF SO_2 BY IPA IMPINGER

Run	Sampling Rate l/min	Source Simulator SO_2 level (ppm)	Method 8 SO_2 Value Analyzed (ppm)	Method 8 Analysis, mg SO_4^{-2}	
				Known Quantity Added	Quantity Found
1	12	500	514	-	-
2	12	1000	1026	-	-
3	12	1000	968	1800	1760
4	12	1000	994	48	48

Runs 1 and 2 demonstrate that SO_2 from the source simulator is not trapped in the 80% IPA impinger after proper purging. During runs 3 and 4, known amounts of sulfuric acid were added to the IPA impinger. Once again, the source simulation was sampled for SO_2. Analysis of the IPA impinger after sampling, with added quantity of SO_4^{-2} even while sampling a source level SO_2. Results were within experimental error.

A high efficiency absorber involves an irreversible chemical reaction, removing the gas molecule from the sample stream. Routinely, the sample train configuration of the Reference Method uses only the first impinger containing the IPA solution for sulfuric acid mist collection. As is well known, the rate of absorption of a gas by a liquid is governed by the conditions prevailing at the interface between the two phases. In

Chemically, the following reaction is believed to occur between SO_3/H_2SO_4 and 80% isopropanol in the first impinger of the sampling train[82]:



$$SO_3/H_2SO_4 + CH_3\text{-}\overset{H}{\underset{OH}{C}}\text{-}CH_3 \longleftrightarrow CH_3\text{-}\overset{H}{\underset{\substack{OH\\ H^+}}{C}}\text{-}CH_3 + SO_4^{-2}$$

The alcohol is acting as a base, accepting a hydrogen ion from the acid to form a protonated alcohol. Note that the reaction is reversible (↔). Consequently, the loss of the hydrogen ion, forcing the reaction to the left, would liberate the SO_3/H_2SO_4 molecule. Any phenomenon that affects this equilibrium would also affect the absorption efficiency of the absorbing solution.

To study this reversible reaction, the National Conuncil for Air and Stream Improvement, Inc. (NCASI)[83] examined the collection efficiency of the Greenburg-Smith impinger containing 80% isopropanol for sulfuric acid mist using a sulfuric acid aerosol generator. The results of the tests are recorded in Table 5-2.

TABLE 5-2

H_2SO_4 CAPTURE EFFICIENCY OF GREENBURG-SMITH IMPINGERS

Run No.	H_2SO_4 Conc., ppm	Flow Rate, lpm	Percent Capture 1st Impinger	Percent Capture 2nd Impinger	Percent Capture 3rd Impinger
1	0.6	6.0	100.0	0	0
2	1.2	7.6	93.4	6.6	0
3	7.7	7.7	97.8	2.2	0
4	78.0	5.8	100.0	0	0
5	78.0	4.7	97.5	2.5	0
6	65.2	2.9	95.4	4.6	0
7	6.6	1.7	96.1	3.9	0
8	10.0	1.5	97.1	2.9	0
9	59.0	1.8	100.0	0	0
		Mean	97.5	2.5	

For nine runs, an average of 97.5 percent of the known amount of sulfuric acid aerosol was captured in the first impinger while that remaining was captured in the second impinger. No acid was found in the third impinger for the entire range of gas flow rates and acid concentrations.

From these findings, NCASI recommends the use of two IPA impingers in the Reference Method instead of one as recommended by U.S. Environmental Protection Agency.

5.1.5 Modified Federal Reference Method 6

Early investigations into sampling methodology for direct sulfuric acid emissions centered around the selective absorption system of Federal Reference Method 8. However, as previously discussed, the Reference Method seemed applicable only to sulfuric acid plants. The system did not have the ability to distinguish between metal sulfates and sulfuric acid vapor. As interest increased in developing a flue gas sampling system that made this differentiation, researchers[84-90] turned their interest to a modification of Federal Reference Method 6 and a refinement of the select IPA absorption method.

Both EPA and Brookhaven National Laboratory have investigated the application of a Modified Federal Reference Method 6 sampling train for monitoring sulfuric acid emissions. The major difference between the two trains is in the collection efficiency of the filtering device for separation of metal sulfates from sulfuric acid vapor. EPA reports its findings as a total water-soluble sulfate (TWSS) fraction and an SO_2 fraction; Brookhaven reports a metal sulfate fraction, a sulfuric acid fraction, a SO_2 fraction, and other gas component fractions.

Several problems have been reported with the use of Modified Federal Reference Method 6 for sulfuric acid emissions determination. The problems encountered focus on four major areas:

- o Sulfate artifact formation on filtering device
- o Potential oxidation of SO_2 in the isopropanol bubbler by contaminants of the presence of metals
- o Residual SO_2 remaining in the isopropanol impinger after proper purging
- o Quantitative separation of sulfuric acid from metal sulfates

5.1.5.1 Sulfate Artifact Formation on Filtering Devices

Sulfate artifact formation on filtering devices has been a major concern for both the Modified Federal Reference Method 6 and the controlled condensation systems. The Brookhaven modification[91] to Federal Reference Method 6 is based on an in-situ isokinetically sized nozzle and quartz fiber filter assembly. This assembly allows the quantitative collection of all metal sulfate particles while permitting sulfuric acid vapor to pass through to the impingers. Not heating the nozzle/filter assembly allows sampling without altering the equilibrium that exists in the stack gas between sulfuric acid vapor and particulate sulfate.

To prevent artifact formation and retention of sulfuric acid on the filter, Brookhaven uses an acid-treated quartz fiber filter that has been shown to pass 95% or more of the flue gas sulfuric acid vapor while collecting nearly 100% of particulate metal sulfates. The trace amount of sulfuric acid retained by the filter is recovered by washing with 100% isopropanol. Consequently, Brookhaven feels that there is no problem with sulfate artifact formation on their filtering device because of the in-situ nature of their system and the pretreatment of the filter pad before use.

In the EPA Modified Federal Reference Method 6 sampling train, the filtering device is a piece of glass wool located in the front portion of the sampling probe. EPA ran a series of tests[92] at a source simulator containing 1500 ppm SO_2 on pyrex and quartz wool plugs used in parallel sampling trains. The test results showed that less than 0.1% of the 1500 ppm SO_2 was being collected on either plug material. Further tests[93] were performed at a 100,000 lb/hr oil-fired boiler to determine if the filtration of flue gas particulate matter during sampling presented an active surface on the probe plug for SO_2 oxidation. These tests involved a series of seven paired samples collected over a two-day period. The results of the measurements are shown in Table 5-3.

Several observations can be made from these data. Although the SO_2 and sulfate levels varied for each run because of fluctuations in steam production, the average sulfate fraction of the total sulfur oxides collected was independent of the probe plug material. It is also apparent that the pyrex plugs retain more sulfate than the quartz plugs. This is probably due to both the greater chemical reactivity of pyrex and its higher surface area. It is interesting to note that the sulfate that penetrates the quartz plug deposits in the probe. Indeed, the bulk of the sulfate fraction was found in the probe wash.

TABLE 5-3
SO_2 AND SO_4^{-2} CONCENTRATIONS MEASURED IN THE FLUE GASES FROM AN OIL-FIRED BOILER

Run	Plug Material	Plug Temperature, °C	Sample Volume (STP),L	SO_4^{-2} ppm v/v				Total SO_4^{-2}	SO_2, ppm v/v
				*pp	PW	IPA	IP		H_2O_2
1	Pyrex	313	29.04	40.7	4.2	3.2	0.9	49.0	840
	Quartz	313	28.75	5.6	26.4	7.9	0.7	40.5	735
2	Pyrex	293	54.82	24.4	5.5	2.3	0.5	32.7	691
	Quartz	293	54.51	6.9	15.1	6.9	0.6	29.5	715
3	Pyrex	264	31.33	26.6	2.9	2.0	0.8	32.3	730
	Pyrex	264	42.22	20.4	3.7	2.5	0.9	27.5	626
4	Quartz	192	26.83	7.9	12.0	4.9	2.5	26.9	678
	Quartz	192	29.04	7.2	12.0	9.0	3.2	31.4	464
5	Quartz	280	26.38	7.0	13.9	6.2	2.2	29.3	729
	Quartz	280	31.07	6.2	17.7	7.5	1.1	32.5	745
6	Quartz	277	28.36	6.0	12.8	4.3	2.8	25.9	640
	Quartz	277	30.03	6.0	13.8	4.5	2.9	27.2	632
7	Quartz	**	29.21	6.0	11.8	5.6	3.0	26.4	620
	Quartz	**	35.04	5.3	13.0	5.3	2.9	26.5	563
Average Pyrex			--	28.0	4.1	2.5	0.8	35.4	722

*Where: PP = probe plug, PW = aqueous probe wash, IPA - isopropanol impinger, IP = impinger plug, H_2O_2 = hydrogen peroxide impinger

**Temperature not monitored.

5.1.5.2 Oxidation of SO_2 within the Isopropanol Impinger

Once the SO_3/H_2SO_4 and SO_2 has passed through the filtering device, the sulfuric acid fraction is absorbed in the first impinger containing 80% isopropanol while the SO_2 is allowed to pass to the hydrogen peroxide impingers. It is within this impinger system that additional problems are encountered. Brookhaven encountered an unknown oxidant in the IPA.[94-95] This oxidant apparently caused a positive error in the sulfuric acid measurement by oxidizing SO_2 dissolved in the 80% IPA impinger. Work by Knoll and Midgett has identified the unknown oxidants as peroxidants and has described a test to determine their product.[96] In other work[97] EPA did not report any problems with oxidation of SO_2 by trace species such as Fe^{+3}, Ni^{+2} or VO^{+2} when they were added to the IPA impinger while sampling known concentrations of SO_2.

Interest in the potential for oxidation of SO_2 by dissolved metal in the isopropanol impinger of the Modified Federal Reference Method 6 sampling train was stimulated during source characterization studies by EPA. In these studies,[98] EPA learned that sulfate levels in the flue gas of oil-fired boilers were much higher than in of coil-fired units of comparable sulfur content. Analysis of particulate emissions from oil-fired boilers indicate that V, S, Ni and Fe are typically the principal metals present in the flue gas. EPA speculated that the metal ions could accumulate in the IPA impinger during sampling and increase artifact formation.

Realizing the potential artifact formation of SO_4^{-2} within the IPA impinger, EPA performed a series of tests to study the oxidation potential of dissolved metals in the 80% IPA impinger. The cations (VO^+, VO^{+2}, Fe^{+3} and Ni) were introduced in the impinger over a range of solution concentrations. Table 5-4 indicates the results of this study.

Table 5-4 shows that neither VO^{+2} nor Ni^{+2} contributes significantly to the potential collection of SO_2 in the 80% IPA isopropanol impinger. The titers from the Barium-thorin titrations for runs 1-6 approached the minimum detectable SO_4^{-2} level. Although the presence of elevated levels of ferric ion did result in increased uptake of SO_2 in IPA, the authors indicated that the levels of interference by iron far exceeded source emission levels typically found at oil-fired boilers.

TABLE 5-4

ARTIFACT FORMATION IN ISOPROPANOL CONTAINING CATIONIC SPECIES

RUN I.D.	Cation	Cation Solution in IPA, g/ml	SO_2 found in H_2O_2, ppm	SO_2 found in IPA, ppm
1	Ni^{+2}	0.37	1031	0.42
2	"	0.49	1026	0.42
3	"	4.17	1039	0.44
4	VO^{+}	0.34	1036	0.68
5	"	3.39	1034	0.84
6	"	6.79	1025	0.60
7	Fe^{+3}	18.60	1028	4.66
8	"	18.60	1033	4.24
9	"	2.23	1033	1.84
10	"	0.13	1040	0.84
11	VO^{+2}	6.79	1041	3.69
	Ni^{+2}	4.17		
	Fe^{+3}	2.23		

5.1.6 Controlled Condensation System

Because of these problems associated with the modified Federal Reference Method 6 sampling system and its inability to distinguish between particulate sulfates and sulfuric acid in the vapor stage, interest turned to the controlled condensation system for monitoring sulfuric acid vapor. The system was designed to sample a gas stream and quantitatively determine the sulfuric acid concentration while minimizing the interference of particulates. This was accomplished through the use of an effective filtering system located either in-situ or external to the gas stream. The main emphasis was to minimize the interaction between the particulate matter and the stack gas sulfuric acid.

5.1.6.1 Controlled Condensation System - Filter Evaluation

Several approaches have been used to facilitate the separation between sulfuric acid and particulate matter, including:

- Out-of-stack filtration[99,100]
- In-stack filtration[101]
- Electrostatic filtrationion[102]

TABLE 5-5

H_2SO_4 VAPOR LOSSES TO FILTER MEDIA AT VARIOUS TEMPERATURES

Source	Temperature, °C	% Loss	Test Conditions	Type of Study
Jain[103]	213	-45%	Method 5 glass fiber filter and holder	Lab
Cheney[104]	150	-13%	ADL/Balstron Microquartz	Field
Peters and Adams[105]	205	-1%	ADL/Balstron Microquartz	Lab
Maddalone[106]	127	-13%	Quartz tube	Lab
	204 - 218	-10%	Quartz wool	Lab
	>254	- 0%	Quartz wool	Lab
	238 - 274	-1.6 to- 7.9%	Quartz filter, holder + Tissue quartz	Lab
	288	-12%	Quartz filter, holder + Tissue quartz + flash (0.13 g/m^3)	
Lundgren[107]	205	-19%	Stainless steel coil + filter (dewpoint 170°C)	Lab
Mitchell[108]	160 - 188	-0-9%	Method 5 Glass fiber filter and holder	Lab/Field
Jain, Blosser, Newport Oglesby[109]	175 - 200	-45%	Method 5 Quartz filter and holder	Lab
Jain, Blosser, Newport Oglesby[110]	>260	- 1%	Method 5 Quartz filter and holder	Lab

5.1.6.1.1 General

The in-stack and out-of-stack filter systems routinely employ a filter pad and a support to retain the particles from the gas stream. Several investigators have examined the effect of temperature, SO_2 concentration, moisture content, and sulfuric acid vapor on clean filter material. The main objective of these investigations was to quantify the amount of sulfate retained by different filter materials and to use the one with the least affinity for sulfuric acid vapor. Table 5-5 lists several investigators who found acid retention on clean filters maintained well above the acid dew point.

Results by Peters[111] indicated that when different filter compositions were challenged with SO_2, temperature, and moisture, the sulfate values found were generally in the range observed for sulfate content on clean filters. However, further tests by Peters[112] indicated that when these same filters were exposed to gas streams containing sulfuric acid vapor in equilibrium with water and SO_2, several filters collected appreciable amounts of sulfates at test temperatures well above the acid dew point. Table 5-6 lists those findings:

TABLE 5-6

SULFUR DIOXIDE - SULFURIC ACID MIST CHALLENGE STUDIES

Filter	Sulfate Gain - mg/M^3				
	Run #				
	1	2	3	Ave.	Std. Dev.
ADL/Balston Microquartz	0	0.2	0.2	0.1	0.1
Gelman Microquartz	0.6	0.5	0.5	0.5	0.1
Reeve Angel 934AH	0.5	0.5	0.5	0.5	0
Whatman GF/A	6.3	6.8	7.3	6.8	0.5
Gelman A	7.0	7.8	8.5	7.8	0.8
Gelman AE	14.4	9.6	15.0	13.0	3.0
MSA 1106BH	12.7	13.3	11.9	12.6	0.7
Reeve Angel 900	13.3	12.8	15.6	13.9	1.5
Schleicher and Schuell 810	15.2	13.7	14.3	14.4	0.8

(Gas Stream/Filter Temperature = 205°C, Moisture Content = 10%, SO_2 = 2000 ppm, H_2SO_4 = 10 ppm)

The results of the test showed that the ADL/Balston microquartz filter retained the least amount of sulfate, while the Gelman and Reeve Angel filters collected a moderate amount, perhaps slightly above background levels. The four borosilicate composition filters collected appreciable levels of sulfates. Peters suggested using a high-purity quartz filter in the controlled condensation system. In conclusion, it was determined that the retention of sulfuric acid by the filter is directly proportional to its glass content. Table 5-7 summarizes these findings.

TABLE 5-7

SUMMARY OF FILTER TEST

Sulfate (mg/M^3)	Grade	Commercial Filters
<1	Quartz	ADL/Balston Microquartz, Gelman Microquartz
	High titania	Reeve Angel 934AH
6-7	Medium titania	Gelman A
	High barium	Whatman GF/A
13-14	Borosilicate	Gelman AE, MSA 1106BH, Reeve Angel 900, Schleicher and Shuell 810

Gelman and Marshall[113] found that SO_2 absorption was the cause of some artifact formation due to the difference in the pH of the various filters. Gelman subjected both quartz and glass fiber filters to standard concenations of SO_2 at elevated temperatures. His study indicated that the quartz filter was non-reactive with SO_2, while the glass fiber filter picked up significant amounts of SO_2. Once again, quartz was recommended as the filter medium.

Maddalone[114] studied the effects of different gas stream compositions of SO_2, moisture, sulfuric acid vapor and % O_2 on the Pallflex Tissue quartz filter pad used in the IERL controlled condensation system. The results of these tests are summarized in Table 5-8. The results of the study indicate that when the gas stream contained only SO_2, H_2O and N_2, no acidity due to sulfuric acid was found on the filter or the following condenser. When sulfuric acid was added to the gas stream, only a slight increase of sulfuric acid concentration appeared on the filter.

TABLE 5-8

EFFECT OF SO_2, H_2O, SULFURIC ACID, AND % O_2 ON QUARTZ FIBER FILTER

Run	Gas Composition				Temperature, °C	Milliequivalents Sulfuric Acid Captured			Milliequivalents Sulfuric Acid Injected
	ppm H_2SO_4	ppm SO_2	%O_2	%H_2O	Filter	Filter	Condenser	Total	
1	1	0	0	7	252	0	0.017	0.017	0.018
2	1	0	0	7	259	0	0.017	0.017	0.019
3	6	0	0	16	257	0.007	0.106	0.113	0.112
4	11	0	0	6	260	0	0.178	0.178	0.195
5	14	0	0	6	257	0	0.244	0.244	0.258
6	14	0	0	6	249	0	0.243	0.243	0.253
7	27	0	0	6	260	0.021	0.425	0.446	0.480
8	28	0	0	14	238	0.013	0.451	0.464	0.509
9	0	2500	0	7	257	0	0	0	0
10	0	2900	0	15	256	0	0	0	0
11	14	1000	0	6	270	0.019	0.320	0.339	0.339
12	16	1100	0	16	261	0	0.260	0.260	0.285
13	15	2100	0	6	274	0.021	0.240	0.261	0.271
14	15	2600	0	16	268	0	0.260	0.260	0/271
15	14	3000	0	6	260	0.013	0.248	0.261	0.262
16	15	3500	0	6	260	0.021	0.216	0.237	0.266
17	5	5400	0	6	271	0	0.160	0.160	0.175
18	0	5200	8	6	254	0	0	0	0
19	14	1100	8	6	271	0.013	0.239	0.242	0.248
20	14	5800	8	6	263	0.012	0.240	0.252	0.249

5.1.6.1.2 Out-of-Stack Filtration

Testing of the out-of-stack heated filter assembly of the controlled condensation system conditioned with fly ash was carried out by several groups. In these experiments, varying amounts of fly ash were placed on the filter (ADL or quartz) before injection of SO_2 and sulfuric acid into the test chamber. Maddalone titrated the fly ash before and after the run to determine if there was any decrease in the alkalinity of the fly ash. By expressing the decrease in the alkalinity in milliequivalents, it could be added to the sulfuric acid vapor recovered from the controlled condensation coil to determine if an acid mass balance was retained. The results of these experiments are summarized in Table 5-9.

The results show that the decrease in fly ash alkalinity could be correlated with the reduction in sulfuric acid vapor seen in the controlled condensation coil. In addition, there was an indication that the presence of SO_2 reduced the percentage of sulfuric acid vapor removed by the particulate matter. Maddalone felt that large concentrations of SO_2 might compete with the sulfuric acid vapor in the gas stream for alkalinity sites on the fly ash and limit the ability of the fly ash to react with the sulfuric acid vapor.

Jain[115] et. al. examined the uptake of sulfuric acid by sodium sulfate (Na_2SO_4)-laden quartz filters in the heated (>260°C) filter holder of the controlled condensation system. The test involved adding particulate Na_2SO_4 to the gas stream containing sulfuric acid and sampling with the quartz filter holder. The results of the test indicated no loss of sulfuric acid on the quartz filter in the presence of Na_2SO_4. Additional testing also indicated minimal losses of H_2SO_4 at the same test conditions using a salt cake typical of particulate emissions from Kraft recovery furnaces instead of Na_2SO_4.

Cheney[116] also investigated the effect of temperature of the quartz filter in association with sulfate distribution in the controlled condensation system. In these field tests, the temperature of the filter was varied while other components of the controlled condensation system remained constant. Duplicate runs were made at five different temperatures.

TABLE 5-9

FLY ASH ALKALINITY STUDY

Run# (Composite)	Filter Temp °C	Gas Composition				Equivalent Fly Ash (g/m^3)	% Sulfuric Acid Found (MEQ)		(MEQ) Total	Total MEQ H_2SO_4 Injected
		ppm H_2SO_4	ppm SO_2	%O_2	%H_2O		Filter	Controlled Condenser		
1	297	9	0	8	4.1	1.3	15(.024)	81(.129)	(.153)	(.169)
2	307	12	650	8	5.3	1.3	14(0.029)	86(.186)	(.215)	(.218)
3	289	11	5300	8	4.7	1.3	11(0.036)	87(.156)	(.182)	(.199)
4	247	11	700	8	4.6	0.13	0(0.000)	87(.169)	(.169)	(.191)

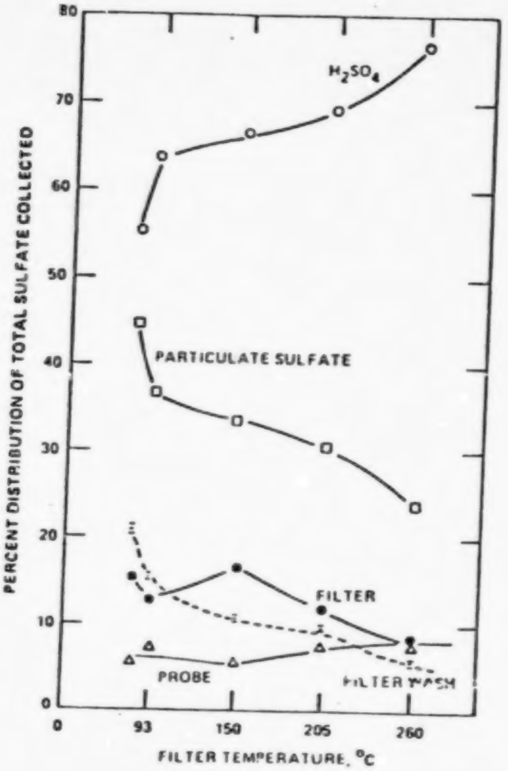


Figure 5-3. Field Studies Involving Sulfate Distribution in the Controlled Condensation System

The results of Cheney's field investigation (Figure 5-3) reveal that there appears to be little sulfate deposition in the probe, which was maintained above 270°C during sampling. However, there is a definite increase in sulfate retention on the filter as the temperature of the filter is decreased from 260°C to 82°C. It is apparent that sulfuric acid is condensing on the filter at the lower temperatures; thus, filter temperature affects the distribution of sulfate within the sampling train.

5.1.6.1.3 In-Stack Filtration

Recently, a study[117] of Federal Reference Methods 5 and 17 filter temperature and its effect on particle catch was undertaken by EPA. The main objective of the study was to investigate the retention of condensible sulfuric acid in both sampling trains and its effect on pollution emission characterization.

The position of the filtering device is the major difference between the two sampling trains. In Modified Reference Method 5 (Figure 5-4), a sample is extracted isokinetically from an effluent stream. The heated filter is located outside the stack, whereas in Modified Federal Reference Method 17 (Figure 5-5) an in-stack filtering system is utilized.

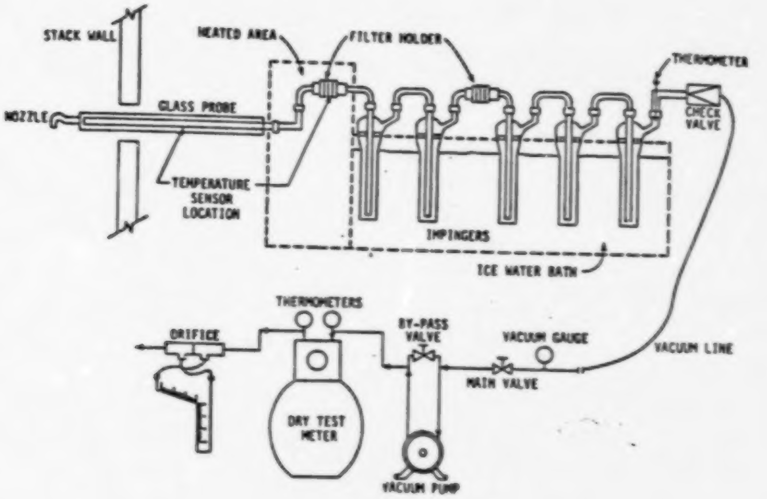


Figure 5-4. Modified Federal Reference Method 5

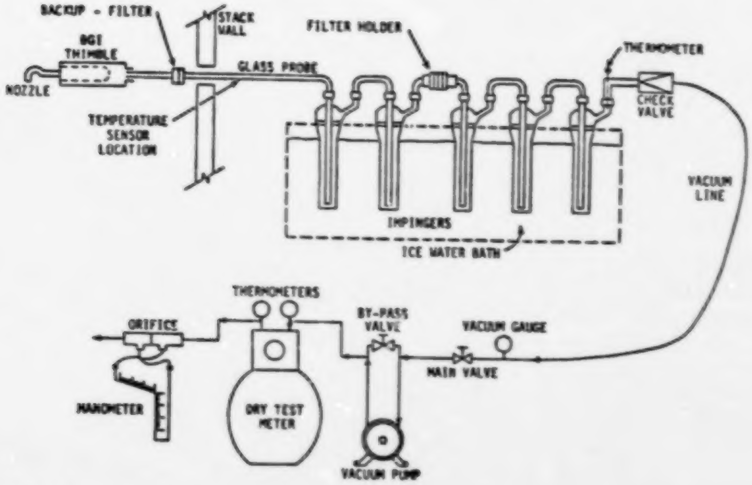


Figure 5-5. Modified Federal Reference Method 17

In Federal Reference Method 17, a sample is extracted isokinetically from the gas stream and filtered in the stack at stack conditions. During the field test, each filter was followed by a complete Reference Method 8 sampling train.

A summary of the sulfuric acid and SO_2 results from the project is presented in Table 5-10.

TABLE 5-10

COMPARATIVE STUDIES: MODIFIED FEDERAL REFERENCE METHODS 5 & 17

Sample Identification	Temperature °C		Filterable Particulate Catch, mg		Sulfuric Acid Mist Condensible mg/M^3	SO_2 mg/M^3
	Stack	Filter	Rinse	Filter		
1-Method 5		320	66	16	33	3612
2-Method 5		320	37	14	41	3346
3-Method 17	156		7	103	28	3430
4-Method 17	156		3	119	22	3413
1-Method 5		320	51	13	46	6817
2-Method 5		320	71	11	38	6787
3-Method 17	159		6	125	30	6794
4-Method 17	159		2	128	26	6325

The distribution of sulfuric acid is distinctly different in the two trains. The M17 train filter was maintained at stack temperature (156-165°C). The table indicates that the in-stack filter characteristically retains a greater amount of acid than the out-of-stack filter, as seen by the catch in the condensible section of the train. In addition, as the temperature of each M5 filter was increased, the amount of H_2SO_4 collected by the filter decreased. Figure 5-6 shows the percent weight loss attributable to sulfuric acid evaporation when the M5 filters were conditioned for 4 hours at the indicated temperatures.

Other observations and conclusions of the report:

- Temperature is the most important variable in sampling methodology with a particulate sulfuric acid system.
- Sulfur oxides appear to condense with particles through either physical or chemical changes on the filtering system.

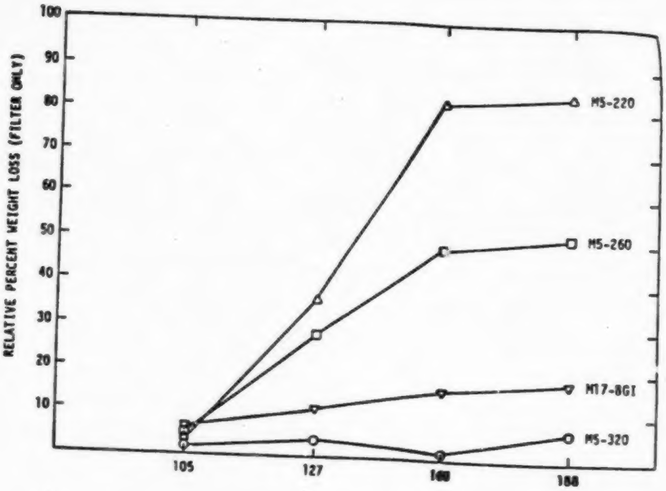


Figure 5-6. Relative Percent Weight Loss vs. Temperature of Method 5 Filters

- More particulate matter was measured by the Method 5 train with filter temperatures at 104°C and 127°C than at higher temperatures of 160°C and 188°C.
- The amount of sulfur oxides collected in the impinger section of the sampling train was higher with Method 5 samples than with the Method 17 samples.
- In all cases, the Method 17 particulate matter catch results was higher than with Method 5 when the external filter was maintained at 160°C.

The retention of sulfuric acid by the filtering device introduces a bias not only in the particulate catch of a Reference Method 5 or 17 train, but also in the sulfate distribution in the controlled condensation system. This reaction of gaseous H_2SO_4 with filtered particles can be either reversible or irreversible. Consequently, careful consideration of the use of an in-stack filter or an out-of-stack filter system is warranted.

Dietz[118] employs an in-stack filter assembly in his controlled condensation sampling train. By employing an in-stack filter assembly, Dietes attempts to maintain the equilibrium that exists, in the stack, between sulfuric acid vapor and particulate matter. However, the data gathered for sulfuric acid and total sulfate emissions at an oil-fired boiler indicated that decreasing the flue gas temperature, and thus the in-stack filter temperature, results in a larger portion of the total sulfate being captured by the in-stack filter. Also, sampling at higher temperatures increases the sulfuric acid fraction captured by the condenser, as demonstrated in Figure 5-7.

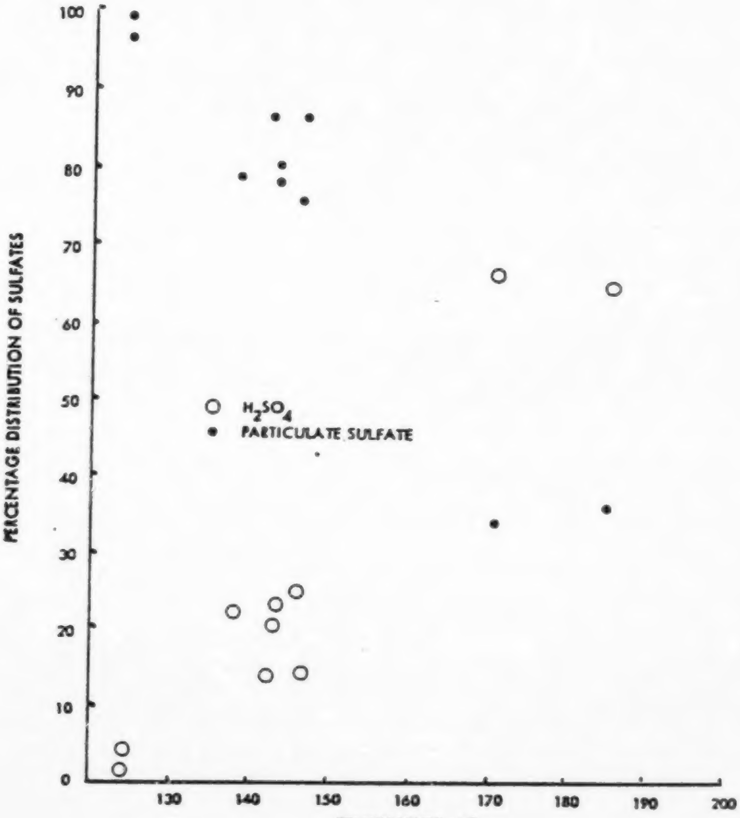


Figure 5-7. Percent Distribution of Sulfates
vs.
In-stack Filter Temperature

5.1.6.1.4 Electrostatic Filtration

The limitations of both the heated out-of-stack filter and the in-stack filter indicated a need for a more efficient and less time-consuming filtering device. Recently, Cheney[119] evaluated a prototype electrostatic precipitator (ESP) that was originally designed by Drinker[120] in 1932. The Drinker precipitator theoretically minimizes the interaction of sulfuric acid and particles during sample extraction. Figure 5-8 demonstrates the construction of the prototype ESP.

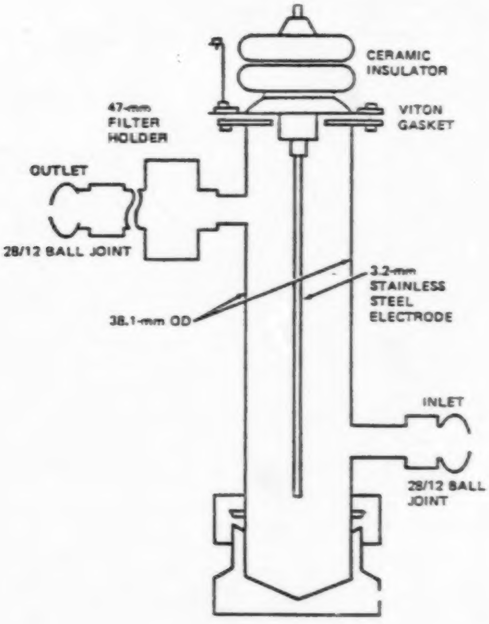


Figure 5-8. Prototype Electrostatic Precipitator

The precipitator underwent both laboratory[121] and field evaluation. Collection efficiency with relationship to particle size, sulfuric acid retention and SO_2 oxidation by the ESP were all investigated.

The results on the collection efficiency of the ESP for ambient air particles are shown in Figure 5-9.

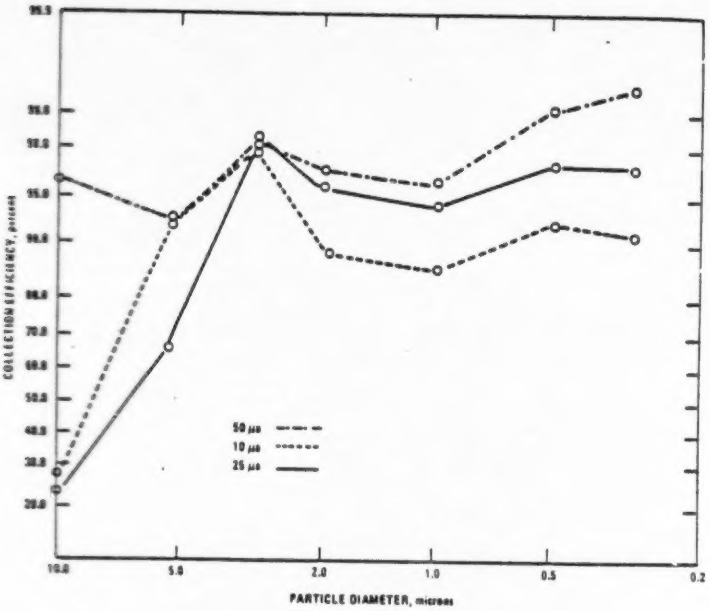


Figure 5-9. Collection Efficiency of Prototype ESP with Ambient Air Particles

As can be seen from Figure 5-9, the voltage applied to the ESP was varied to determine its effect on collection efficiency. Collection efficiency at 50 μamps was greater than 95% for all sizes (0.3 to 10 μm).

Additional tests were performed by Cheney at a 100,000 lb/hr ESP controlled oil-fired steam boiler. The sampling system consisted of a high-temperature quartz probe, a high temperature ESP with back-up high temperature quartz filter, and a continuous sulfuric acid mist monitor (SAMM) (Figure 5-10).

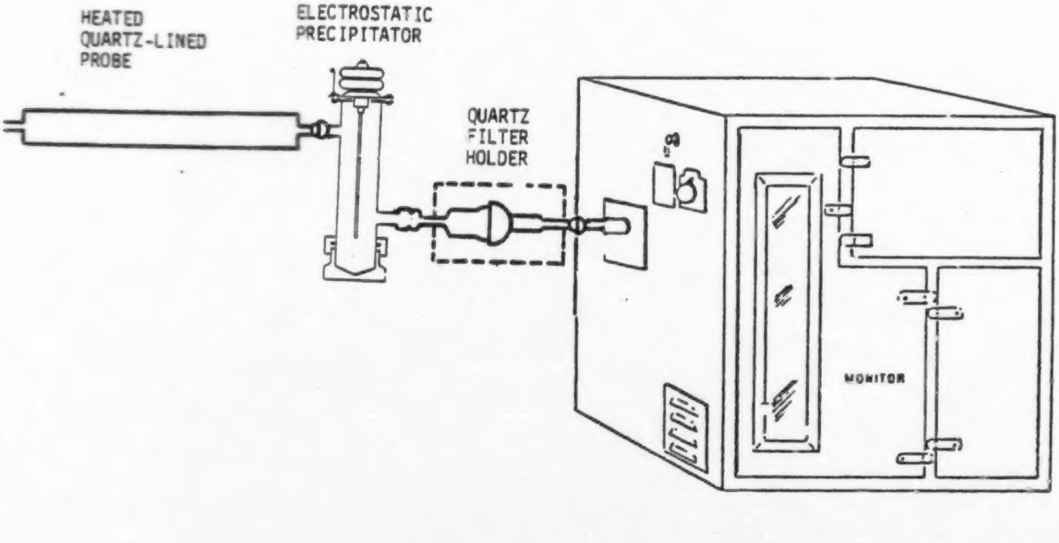


Figure 5-10. Prototype ESP and SAMM System

During sampling, the probe and ESP-filter temperatures were 343°C (650°F) and 332°C (630°F) respectively. After sampling, those fractions of the sampling train analyzed were extracted with both isopropanol and water for a total sulfate determination. Table 5-11 indicates the results of this test. There appears to be little significant retention of H_2SO_4 by any part of the sampling train.

TABLE 5-11

SULFATE DISTRIBUTION IN THE PROTOTYPE ESP/SAMM SYSTEM

Component	Sulfuric Acid Concentration PPM			
	Run No. 1		Run No. 2	
	IPA	H_2O_4	IPA	H_2O
Probe	0.5	0.6	<0.5	<0.5
ESP	0.5	4.6	<0.5	4.3
Filter and Holder	<0.5	<0.5	<0.5	<0.5
SAMM[1]	15.5	--	13.8	--

[1] Assumed to be H_2SO_4 from conductivity.

Laboratory studies were also undertaken by EPA and NCASI to determine whether the ESP caused oxidation of SO_2 to sulfate. The oxidation of SO_2 by the ESP could possibly occur by two mechanisms: (1) high temperature conversion of SO_2 by metal salts captured by the ESP, and (2) oxidation by electrical discharge. EPA tested the ESP at ambient temperature, while NCASI tested the unit at greater than 500°F. Both results, as shown in Table 5-12 indicated minimal conversion of SO_2 to SO_3 while passing known concentrations of SO_2 through the system.

TABLE 5-12

OXIDATION OF SO_2 TO SO_3 USING A PROTOTYPE ELECTROSTATIC PRECIPITATOR

Sample #	Gas Stream Temperature	SO_2 Concentration, ppm	SO_3/H_2SO_4 Concentration, ppm
1	>260°C (>500°F)	36	0
2	>260°C (>500°F)	39	0
3	>260°C (>500°F)	439	0
4	>260°C (>500°F)	347	0
5	Ambient	1000	2.1
6	Ambient	1000	1.2
7	Ambient	1000	0.8
8	Ambient	1000	0.8

NCASI field tested[122] the prototype ESP at a Kraft recovery furnace following an industrial electrostatic precipitator. This field test determined the prototype ESP to be 99.3 percent efficient in collecting particles down to 0.2 at a flow rate of 10 lpm.

5.1.6.2 Controlled Condensation System - Collection Efficiency of Goksoyr/Ross Condenser

Historically, the detection of sulfuric acid has been accomplished through the select condensation method using the Goksoyr/Ross condenser. As discussed earlier, the stack gas is extracted from the source through a heated glass probe and filter assembly, both maintained at 287°C (550°F). The particulate matter is separated from the gas stream, by the filter assembly and passes through to the condenser. As the gas passes through the condenser, its temperature is reduced to below the dew point of sulfuric acid, yet above the dew point of water. As indicated by Figure 5-11, this temperature range is fairly broad.

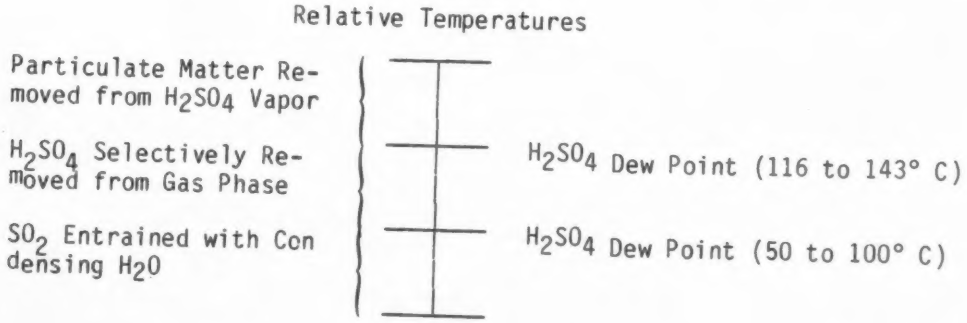

Relative Temperatures
Particulate Matter Removed from H_2SO_4 Vapor
H_2SO_4 Selectively Removed from Gas Phase
SO_2 Entrained with Condensing H_2O
H_2SO_4 Dew Point (116 to 143° C)
H_2SO_4 Dew Point (50 to 100° C)

Figure 5-11. Dew Point Range For Water and Sulfuric Acid

As the gas is cooled, the sulfuric acid vapor is condensed and collected on the walls of the cooling coils or on a backup frit of the condenser. The temperature of the condenser allows SO_2 to pass and water vapor to be collected in an impinger assembly following the condenser.

The collection efficiency of the Goksoyr/Ross coil has been examined by many researchers.[123-126] Both laboratory and field evaluation have determined that the Goksoyr/Ross coil and frit assembly can effectively capture >90% of sulfuric acid vapor in the flue gas stream.

Collection efficiency studies in the laboratory routinely involve a sulfuric acid vapor generator to provide a known concentration of the pollutant (Appendix A). Known concentrations of SO_2 and moisture are generated to provide a true characteristic source emission.

Jain, in his laboratory evaluation of the controlled condensation condenser, produced four different levels of sulfuric acid vapor to determine if there were any effects of varying acid concentration on percent of capture. All tests were performed at a flow rate of approximately 9 lpm. Table 5-13 displays the results of these tests, which show that the efficiency of capture was generally higher than 95%.

TABLE 5-13

EFFECT OF H_2SO_4 CONCENTRATION ON CAPTURE EFFICIENCY ON GOKSOYR/ROSS COIL

H_2SO_4 Conc. (ppm)	No. of Runs	% H_2SO_4 Capture		
		Max.	Min.	Avg.
1	6	99.2	92.0	95.0
5	4	99.4	94.7	97.8
20	1	95.9	95.9	95.9
50	2	91.7	91.1	91.4

Similar results were also recorded by Maddalone[127] and co-workers in their laboratory evaluation of the Goksoyr/Ross coil. In these tests, known concentrations of sulfuric acid vapor were produced by a sulfuric acid vapor generator. In addition, a pyrex wool plug was inserted at the entrance of the condenser to approximate a particle control device. The results of these tests (see Table 5-14) indicated that the collection efficiency of the Goksoyr/Ross coil did not vary greatly over the range of percent H_2O, condenser temperature or sulfuric acid concentration.

When the pyrex wool plug temperature was maintained in excess of 254°C no H_2SO_4 was found on the plug after testing. Also, temperatures >280°C did not adversely effect the total recovery of sulfuric acid vapor in the Goksoyr/Ross coil. The overall average recovery of the coil was 95% with a coefficient of variation of ± 6.7%.

Lisle[128] also conducted additional studies in which nearly complete sulfuric acid recovery (>99.5%) was achieved when the condenser was maintained at 60°C. These tests were performed with synthetic flue gas mixtures containing sulfuric acid vapor (0-35 ppm), nitrogen (82.8%), carbon dioxide (15%), oxygen (2%), and sulfur dioxide (2,000 ppm).

The collection efficiency of a coil can also be determined experimentally by applying Stokes' Law. When a gas stream containing dispersed liquid droplets is passed through a coil, some droplets are centrifuged onto the walls of the coil. Stokes' gives the radius needed for the liquid droplet to be deposited on the coil walls by the following equation[129]:

$$r = [9\, w \mu / 2a\, (\rho - \sigma)]^{0.5},$$

where:

r = droplet radius, cm
w = radial velocity required to move droplet to wall, cm/sec
  = $4\, Qx/n^{-2} D\, d^2$, where
  Q = gas sampling rate, cc/sec
  x = distance moved by droplet to wall, cm
  n = number of turns in coil
  D = coil diameter, cm
  d = tube diameter, cm
μ = gas viscosity, g/cm-sec
a = radial acceleration of gas stream, cm/sec^2, = $32\, Q^2/\pi^2 d^4 D$
ρ = density of acid aerosol, g/cc
σ = density of air

TABLE 5-14

COLLECTION EFFICIENCY OF GOKSOYR/ROSS CONDENSER UNDER VARYING SULFURIC ACID AND MOISTURE CONCENTRATIONS

Run #	Gas Composition			Component Temperature, °C		Sulfuric Acid	Sulfuric Acid Recovered MEQ/(%)	
	H_2SO_4 ppm	% H_2O	Particulate Matter, g	Pyrex Wool Plug	Condenser	Generated MEQ	Pyrex wool Plug	Condenser
1	17	7	0	204	44	0.238	0	0.225/94.5
2	11	5	0	288	41	0.207	0	0.207/100.0
3	13	5	0	254	46	0.234	0	0.213/91.0
4	10	4	0	286	47	0.179	0	0.200/111.7
5	10	4	0	281	45	0.185	0	0.171/92.4
6	12	5	0	275	35	0.214	0	0.209/97.7
7	11	5	0	254	43	0.205	0	0.193/94.1

Since the density of air is small compared to the density of the acid aerosol, ρ, the above equation can be rewritten:

$$r = (9\, w\, \mu / 2 a \rho)^{0.5}$$

When values for a and w are substituted into the above equation, we have:

$$r = (9\, \mu\, x d^2 / 16\, n \rho Q)^{0.5}$$

When $X \longrightarrow 0$, $r \longrightarrow 0$, and $x = d$, then

$$r = (9\, \mu d^3 / 16 n \rho Q)^{0.5}$$

Hence, for each value of X, droplets of radius r and greater will reach the collecting wall.

In their original work, Goksoyr/Ross used a 4 mm O.D. coil to trap out sulfuric acid droplets. Applying Stokes' Law, the calculations indicate that all droplets of diameter greater than 1.26μ entering the coil at maximum distance (tube center) from the collecting wall would settle out on the collecting walls of the coil for a 20-turn coil. Smaller acid particles ($<1\ \mu$) would likely agglomerate and be thrown to the walls of the condenser.

Since sulfuric acid mist has a particle size diameter range from 0.5 to 10 μ in size (Figure 5-12) and to ensure maximum sulfuric acid recovery.

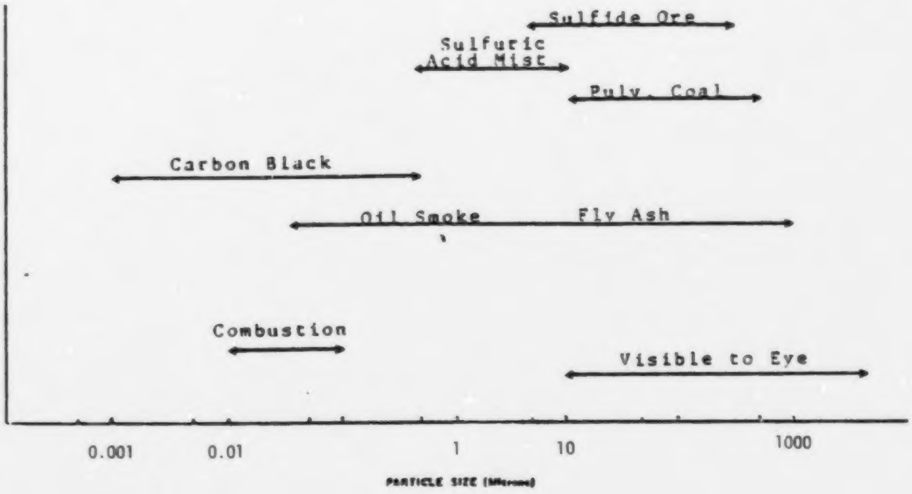


Figure 5-12. Sulfuric Acid Mist Particle Size

Goksoyr/Ross inserted a frit at the end of the coils to retain any acid aerosol escaping the condenser coils. Smaller acid particles (<1.0 µ) are likely to agglomerate and be thrown to the walls of the condenser.

Stokes' Law further predicts that decreasing the tube diameter of the condenser should increase its collection efficiency. However, the lower size of the tube diameter is limited by Reynolds number, pressure drop across the system and decrease in cooling capacity of the condenser itself. Recently, Maddalone and Cheney used a large 7 mm O.D. diameter coil in their sampling system. The larger size of the condenser coil would enable more of the particles to traverse the coils to be captured by the backup frit, leading to increased frit plugging.

Recently, several authors[130,131] have observed plugging of the frit in the condenser assembly. Such plugging could be associated with (1) particles escaping the preceeding high temperature filtering device and becoming embedded in the frit and (2) small (<1 µ) sulfuric acid particles escaping the coils and condensing on the frit. Repeated field application of the Goksoyr/Ross condensor with back-up frit has increased plugging, the more the frit becomes plugged, thus increasing pressure drop across the total system to the point of rendering it useless.

Recently, Winberry and Dellinger[132] examined the unknown material lodging on plugged frits by electron microscopy and X-ray fluorescence. These tests indicated the presence of silica, iron, zinc, calcium, and sulfur. Figure 5-13 is a photograph taken by the electron miscroscope of the embedded material in the frit. Figure 5-14 shows the chemical analysis of that embedded material.

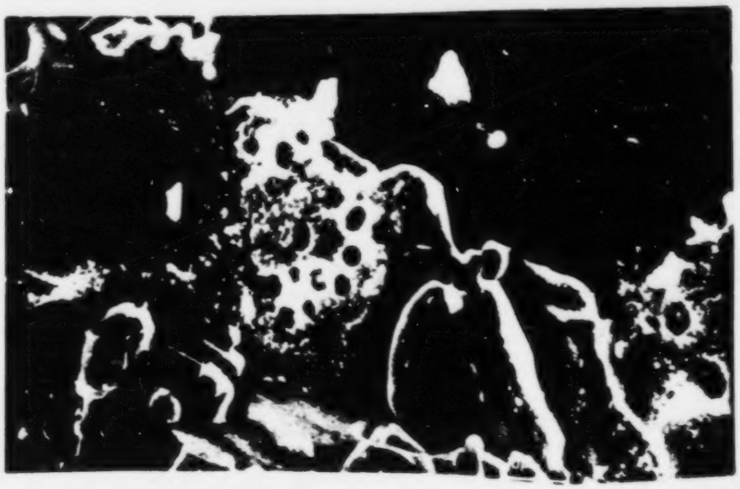


Figure 5-13. Electron Microscopy Enhancement of Embedded

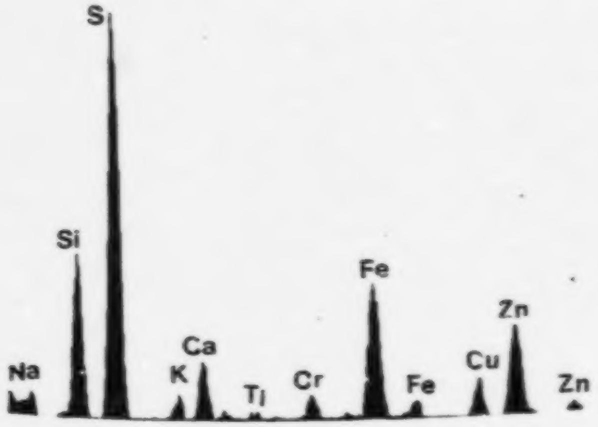


Figure 5-14. Chemical Analysis by Electron Microscope and X-Ray Fluorescence of Embedded Material in Frit

The report concluded the material causing the frit to plug was either circumventing the heated prefilter and plugging the frit as particulate matter or the material was in the gas phase at the prefilter, and then condensed on the frit at condenser temperature. Unfortunately, the analytical techniques employed in the investigation could not determine the exact composition of the embedded material.

When the frit becomes plugged, the sampling rate decreases as the pressure drop across the total sampling system increases, thus lowering collection efficiency of the sampling train. Recent tests have demonstrated that the collection efficiency of the Goksoyr/Ross coil is dependent upon the sampling rate of flue gas pulled through the sampling train.

Stokes' equation once again dictates a direct relationship between the radius of sulfuric acid vapor droplets, sampling rate, and collection efficiency of the sampling train. This, in turn, affects the ability to distinguish between particulate sulfate and sulfuric acid vapor in the controlled condensation system. Numerous investigators have examined sulfate distribution throughout the sampling train as it relates to sampling rate. Cheney[133] varied the flow rate through the sampling train and analyzed for sulfate in each component of the train. The results of this investigation are indicated in Table 5-15.

TABLE 5-15

SULFATE DISTRIBUTION AND SAMPLING RATE WITH GOKSOYR/ROSS CONDENSER

Sample Rate (l/min)	Total Sulfate Collected ppm	% Total Sulfate Captured		
		Probe	Quartz Filter	Condenser
16.0	36.3	10.7	9.9	79.3
12.0	38.6	13.9	7.8	78.4
8.3	35.8	12.3	13.9	73.8
7.5	31.6	13.6	16.8	69.6
6.5	27.2	15.8	17.8	66.4
5.1	41.9	18.3	10.6	71.1
4.7	37.8	36.0	12.2	51.8
3.8	32.8	19.1	30.0	50.9
2.3	50.1	23.9	36.9	39.2

As indicated by the table, at the slower flow rate, more of the sulfate is deposited in the probe or filter portion of the train, thus decreasing collection efficiency of the Goksoyr/Ross condenser. Furthermore, retention of sulfuric acid by particles can be demonstrated by the marked decrease of percent acid captured in the condenser at lower flow rates. As the flow rate increases, the amount of acid penetrating the probe and filter increases until a plateau is reached between 12 and 16 l/min (see Figure 5-15).

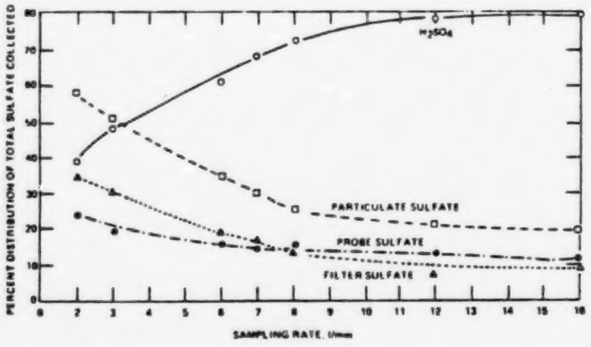


Figure 5-15. Effect of Sampling Rate on Sulfate Distribution

Between 12 and 16 l/min, there appears to be little effect of flow rate on sulfate distribution to the probe or filter assembly. At the lower flow rate of 2 to 6 l/min, the steeper slope of filter catch indicates that the sulfuric acid is being collected in the front half of the train, predominantly at the filter, with a lesser retention by the probe.

Because of the problem of frit plugging, resulting in increased pressure drop across the sampling system, and because of the bulkiness of the condenser itself, Cheney investigated a replacement for the sulfuric acid collector. Pyrex wool was shown to be an excellent collector of sulfuric acid in the probe plug study for the Modified Federal Reference Method 6. Cheney constructed a special temperature controlled glass wool plug holder to replace the Goksoyr/Ross coil condenser, as shown in Figure 5-16.

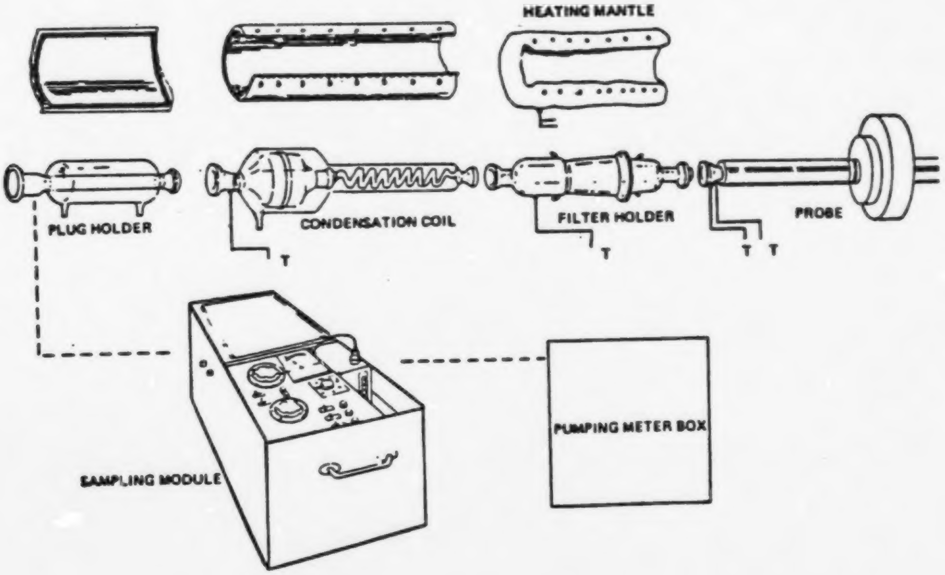


Figure 5-16. Special Plug for Sulfuric Acid Mist Monitoring

During initial evaluation the sampling system consisted of a heated quartz probe (>276°C), a heated quartz filter holder (>276°C) containing a high-purity quartz filter (99.9% effective for collecting particle sizes down to 0.3 μm), temperature controlled Goksoyr/Ross condensor with back-up frit, the special temperature controlled (70°C) glass wool plug, and a series of Greenburg-Smith impingers immersed in an ice bath. The first impinger containing 80% isopropanol collects sulfuric acid mist and vapor that penetrates the special plug, while the next two impingers contain 10% hydrogen peroxide for collection of sulfur dioxide. After the impingers was a meter box assembly containing a dry gas meter, a pump, and temperature monitoring devices.

Two series of field tests were performed to demonstrate collection efficiency of (1) the Goksoyr/Ross condenser, and (2) an equivalent sulfuric acid vapor collector. Both field experiments were performed on a 100,000 lb/hr oil-fired steam boiler burning a nominal 2.2% sulfur fuel oil containing 350 ppm vanadium.

During the first series of field tests, the Goksoyr/Ross condenser was used as the primary sulfuric acid aerosol collector, followed by the special glass wool plug (Figure 5-16). Both the condenser and plug were maintained at 60°C. The results of these measurements are presented in Table 5-16.

TABLE 5-16

TOTAL SULFATE WITH AND WITHOUT SPECIAL GLASS WOOL PLUG HOLDER

Sample	Total Sulfates, ppm				SO_2 ppm	% Total	
	Probe Plug	Heated Quartz Filter	Condenser	Special Glass Wool Plug		With Condenser	With Condenser and Special Glass Wool Plug
1	4.4	5.0	25.6	0.4	824	4.12	4.16
2	4.3	5.3	21.2	0.7	745	3.98	4.16
3	6.9	5.4	26.5	0.7	944	4.21	4.28
4	8.4	3.5	26.8	1.6	805	4.72	4.90
5	8.9	4.1	21.7	2.7	768	4.49	4.81
6	4.2	6.9	21.2	2.8	717	4.37	4.73

$\%T = (\text{Total } SO_4^{-2})/(\text{Total } SO_4^{-2} + SO_2) \times 100$, ppm

Apparently little acid penetrated the coil and frit. However, a slight increase in percent conversion was noted as the samples were extracted in chronological order of collection.

The final series of tests involved extracting a sample with the condenser in place, then removing the condenser and replacing it with the special glass wool plug. The results of twelve extractions (six with condenser, six with special glass wool plug) are presented in Table 5-17.

TABLE 5-17

ACID COLLECTION WITH CONDENSER AND SPECIAL GLASS WOOL PLUG

Condenser			Glass Plug		
Sulfate ppm	SO_2 ppm	% T	Sulfate ppm	SO_2 ppm	%-T
35.5	824	4.17	31.5	707	4.27
31.6	745	4.07	37.8	896	4.05
42.2	944	4.28	58.5	858	4.38
41.5	805	4.90	33.7	777	4.16
38.8	768	4.81	30.7	649	4.52
35.6	717	4.73	31.3	728	4.12

% T = (Total SO_4^{-2})/(Total SO_4^{-2} + SO_2) x 100, ppm

There appears to be no difference in the collection efficiency of the two sampling trains, as the average values are recorded in Table 5-18 from Table 5-17 values.

TABLE 5-18

AVERAGE ACID COLLECTION WITH CONDENSER AND SPECIAL GLASS WOOL PLUG

Component	Total Sulfates Collected ppm	Total SO_2 ppm	% T
Condenser	37.5 ± 3.4	801 ± 57	4.49 ± 0.32
Special Glass Wool Plug	37.4 ± 7.4	769 ± 58	4.58 ± 0.43

% T = (Total SO_4^{-2})/(Total SO_4^{-2} + SO_2) x 100, ppm

5.1.7 Sulfuric Acid Mist Monitor (SAMM)

The Sulfuric Acid Mist Monitor extracts a sample from the gas stream, condenses out the sulfuric acid in a modified Goksoyr/Ross coil, and records the concentration by rinsing the condenser with an isopropanol/water solution into a conductivity cell which measures the conductivity of the sulfuric acid-water solution. The conductivity is directly proportional to the concentration of the sulfuric acid vapor in the gas stream.

As with other sulfuric acid vapor continuous emission monitoring systems, the SAMM system has had very little field evaluation. The prototype was field tested at a sulfuric acid plant and the present monitor has been evaluated at a coal and oil-fired utility.

Laboratory evaluation of the monitor indicated that it had the ability to detect sulfuric acid vapor from a sulfuric acid generator with a satisfactory degree of reproducibility. The Relative Standard Deviation (RSD) for this system was about 10% at sulfuric acid concentrations of 5 to 15 ppm.

However, when the monitor tested in the field, it did not perform as accurately as laboratory evaluation indicated. The system was found to be bulky and heavy, and it required precise orientation at the sampling port for proper operation. In addition, because of its electronics package, full time attention was required to keep it operating.

As with other systems, the need for a good particulate removal device was imperative to maintain a proper monitor operation. If particles are allowed to enter the condenser, they will soon plug the frit or glass wool plug and interfere with the measurement cell. Other system failures that occurred during field testing included the following:

- Refrigeration system
- Mass flow controller
- Reagent inventory

5.1.8 Severn Science Limited SO_3 Monitor

The Severn Science Limited SO_3 Monitor automatically samples gases, and detects and records the SO_3 concentration in the gas stream continuously through wet chemical analysis and photometric methods. The photometer in the monitor develops an output voltage directly proportional to the SO_3 concentration in the gas stream.

Monitors of this design have been used extensively in a number of power plants in England, western Europe, and, more recently, in the United States. The monitor has performed so well in England that it is recommended by the Central Electric Generating Board as the normal method of analysis for SO_3 in flue gas.

Very little information is available on problems associated with long term usage of this monitor in the United States. Common problems encountered with the SSL monitor include sudden large acid spikes, dissolved oxygen in isopropanol, and reaction bed aand isopropanol light refraction characteristics.

5.1.8.1 Sudden Large Acid Spikes

In several field tests, sudden large acid spikes would appear on the recorder even when the flue gas SO_3 concentration remained constant. Historically, such spikes have been attributed to sulfuric acid condensing on cold spots in the probe and then breaking loose to be recorded as sulfuric acid vapor emissions. This is especially likely at the moment the probe is removed or inserted into the stack gas. Under normal conditions, the probe tube is held at 200°C (392°F) or higher, which is well above the dew point. Consequently, sulfuric acid should not condense on the inner surfaces of the sampling probe.

5.1.8.2 Dissolved Oxygen in the 80% Isopropanol Absorbing Solution

One of the major problems associated with detecting a pollutant by means of a flow through cell is interference of gas bubbles in the liquid stream. Bubbles in the cuvette of a flow-through photometer can cause erroneous readings. The source of this interference has been traced to dissolved oxygen in the 80% isopropanol solution used in the monitor. This problem has been corrected by storing the 80% isopropanol solution at ambient temperature (20°C). At this temperature, all of the oxygen will have been driven off by the time the solution is used.

5.1.8.3 Reaction Bed

The heart of the monitor is the reaction of the isopropanol-sulfuric acid solution with the resin bed of barium chloranilate to form a purple solution of acid choranilate ion and a precipate of barium sulfate which remains on the bed. If channeling occurs on the resin bed, the isopropanol-sulfuric acid soluton will pass down only one side of the bed, causing the barium sulfate to form quickly on that side. This increases the possibility of these crystals breaking lose and lodging in the cuvette of the flow-through photometer, once again causing spurious readings.

5.1.8.4 Isopropanol Light Refraction Characteristics

The temperature of the isopropanol flowing thorugh the measuring cuvette must be constant or the light refraction characteristics of the solution will change, altering the calibration curve. It is important that the temperature of the isopropanol solution flowing into the cuvette be the same during sampling and calibration.

6.0 SULFURIC ACID MONITORING SYSTEMS - COMPARATIVE LABORATORY AND FIELD STUDIES

Because sulfuric acid emissions from stationary sources are not regulated, there has been very little effort to standardize an analytical technique for their detection. What little effort there has been in standardization is due, in part, to the corrosive nature of H_2SO_4 to plant duct work. Consequently, there have been few comparative or collaborative studies involving sampling methodology for monitoring sulfuric acid emissions. Table 6-1 lists those investigators and analytical methods used to compare monitoring systems. Most interest has centered around the controlled condensation system and the Federal Reference Method 8 procedure.

6.1 Comparative Studies

6.1.1 Modified Federal Reference Method 6/Controlled Condensation System/Acid Dew Point Meter

Field measurements were conducted by EPA of emissions of primary sulfates from oil-fired boilers procedures: (1) Modified Federal Reference Method 6, (2) controlled condensation system, and (3) acid dew point meter.[134] The field measurements were performed over a five-day period at excess oxygen levels from 0.2% to 1.0%.

Total sulfate was determined from the Modified Federal Reference Method 6 train by collecting and analyzing the probe plug, probe wash, IPA impinger, and impinger plug. SO_2 was determined by analyzing the hydrogen peroxide impinger. Total sulfate in the controlled condensation system was determined by analysis of the probe wash, filter and holder, condenser, transfer line and IPA impinger. The H_2O_2 impinger was also analyzed for SO_2. Additionally the sulfuric acid vapor content of the gas stream was determined by the acid dew point meter. A summary of the field measurements results is presented in Table 6-2.

TABLE 6-1. SULFURIC ACID MIST MONITORING: COMPARATIVE STUDIES

Operator	Year	Experimental Conditions	Pamameters Monitored								
Goksoyr/Ross	1961	Laboratory Experiment	SO_3/H_2SO_4			X			X		
Goksoyr/Ross	1962	Laboratory Experiment	SO_3/H_2SO_4			X			X		
British Petroleum	1963	Laboratory Experiment	SO_3			X			X		
British Petroleum	1965	Heavy Fuel Oil/air Flame	SO_3			X			X		
Engel	1978	Diesel Exhaust	SO_3/H_2SO_4	X	X				X		
Cheney/Fortune Homolya/Barnes	1978	FFFSG	$MSO_4/SO_2/H_2SO_4/SO_3$	X					X		
Cheney/Homolya	1978	FFFSG	$MSO_4/SO_2/H_2SO_4$			X		X			
Cheney/Homolya/ Barnes	1979	FFFSG	H_2SO_4/MSO_4	X		X	X				
ENEL (Italian Utility)	1979	Heavy Fuel Oil/Air Flame	H_2SO_4			X			X		
Homolya/Cheney	1979	FFFSG with Limestone Scrubber	$H_2SO_4/MSO_4/SO_2$			X	X				
Cheney/Eaton	1979	Sulfuric Acid Plant	H_2SO_4						X	X	
Pearson/Mantz	1979	FFFSG	H_2SO_4			X					X
Fields, Jackson & Raask	1980	FFFSG	H_2SO_4		X				X		
Jackson, Weight Hotchkiss	1980	Laboratory Experiment	H_2SO_4		X				X		
Severn Science Ltd.	1981	Sulfuric Acid Generator + Water	H_2SO_4		X	X					
Dickson	1982	FFFSG With Scrubber	H_2SO_4		X			X		X	

TABLE 6-2

COMPARATIVE STUDIES

Test Day	Excess Oxygen %	Total Sulfates, ppm v/v		Acid Dew Point Meter Gaseous H_2SO_4, ppm
		Modified Method 6	Controlled Condensation System	
1	1.0	56.1	35.2	56.1
2	0.6	46.5	29.9	34.0
3	0.4	34.3	12.3	1.0
4	0.3	26.7	13.0	9.2
5	0.2	21.2	9.3	-

The best agreement was found between Modified Federal Reference Method 6 and the acid dew point meter. Apparently, as the excess O_2 decreased, there was a greater population of particles available to scavange the sulfuric acid from the flue gas. Total sulfates measured by Modified Federal Reference Method 6, that are reported as gaseous sulfuric acid by the dew point meter, decreased with decreasing O_2. No explanation was offered for the lower sulfate results obtained with the controlled condensation system.

Further comparison of the acid fraction (less probe and filter) of Modified Federal Reference Method 6 to the controlled condensation system is shown in Table 6-3.

TABLE 6-3

SULFURIC ACID SULFATE

Test Day	Excess Oxygen %	Sulfuric Acid Sulfate, ppm v/v*	
		Modified Method 6	Controlled Condensation System
1	1.0	17.0	23.2
2	0.6	19.9	19.7
3	0.4	12.1	5.4
4	0.3	10.3	7.3
5	0.2	5.7	4.2

* Sulfuric Acid Sulfate = [Total Sulfate]-[Probe and Filter Sulfate]

The sulfuric acid sulfate fraction results agree reasonably well for the two analytical procedures. As we expected, the sulfuric acid sulfate fraction increased with an increase in excess oxygen.

6.1.2 Controlled Condensation System/Federal Reference Method 8/Dew Point Meter

KVB, Inc. has long studied emissions from industrial boilers, gas turbines, and industrial processes utilizing continuous and wet chemical methods for monitoring sulfur dioxide, sulfuric acid vapor, and total sulfate.[135-141]

One study at a gas turbine compared the controlled condensation system, Federal Reference Method 8, and the dew point meter. Results of this study, Figure 6-1, indicate a close correlation between Federal Reference Method 8 and the controlled condensation system.

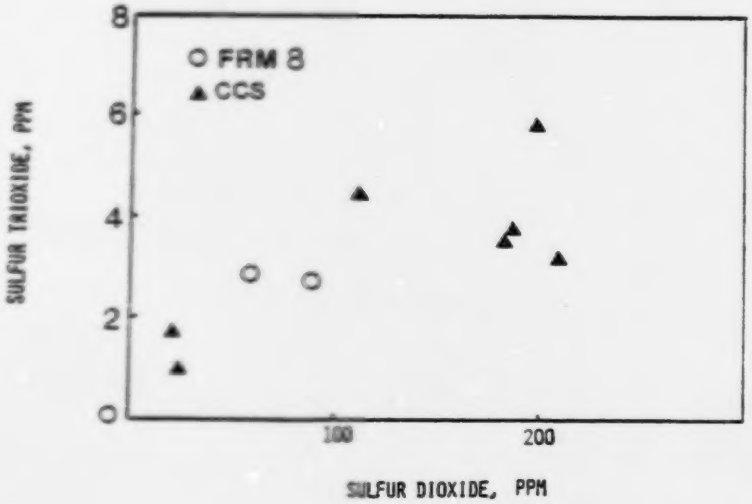


Figure 6-1. Comparative Studies: Controlled Condensation System and Federal Reference Method 8

In addition, values for sulfuric acid vapor, as reported by the controlled condensation system, were used in conjunction with measured moisture to calculate a dew point temperature from Muller's Theoretical Des Point curve. These calculated dew point temperatures correlated closely with the dew point temperatures measured by the dew point probe.

6.1.3 Severn Science Limited/Sulfuric Acid Mist Monitor/Miniature Acid Condensation System

Recently, Dickson[142] of Southern Research Institute evaluated the both laboratory and field application performance of three sulfuric acid vapor sampling systems. The systems evaluated in this study included the Severn Science Limited continuous sulfuric acid vapor monitor; the automated prototype Sulfuric Acid Mist Monitor (SAMM) developed by EPA; and a miniature-acid condensation system (MACS), also developed by EPA. The operational characteristics of each system were investigated both in the laboratory, using a thermal generator as a source of sulfuric acid vapor, and in the field at the inlet and outlet of an electrostatic precipitator located at a coal-fired power plant.

The laboratory evaluation of the program indicated that there was excellent agreement between the three systems when measuring known concentrations (2 to 20 ppm) of sulfuric acid vapor from the generator. The relative standard deviation (RSD) for the SAMM system was about 10% at a sulfuric acid concentration of 5 to 15 ppm. Likewise, the RSD for the MACS system was less than 5% at the 10 to 20 ppm level and less than 10% at the 2 to 4 ppm level. Results for the SSL monitor indicated less than favorable response at the 4 ppm level from the sulfuric acid generator; however, better agrement was achieved at the 5 and 10 ppm levels.

Field evaluation of the systems showed relatively good agreement over a ten day test period. In general, Dickson found the MACS system the easiest to operate and, because of the flexibility of the umbilical line, adaptable for sampling in a variety of locations. The prototype SAMM system was bulky, heavy, and required precise positioning for sampling.

The average daily sulfuric acid vapor concentrations obtained from the three systems at the inlet and outlet of the ESP are shown in Figures 6-2 and 6-3.

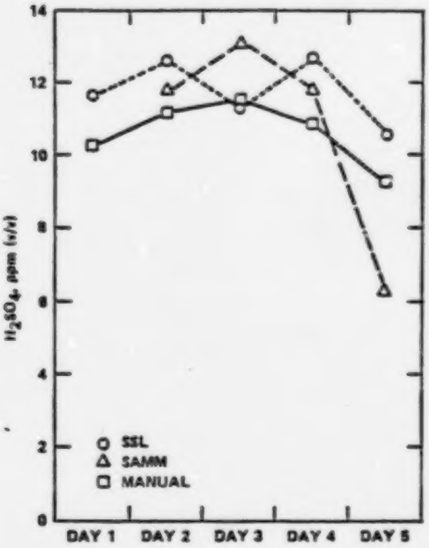


Figure 6-2. Comparative Studies: Inlet

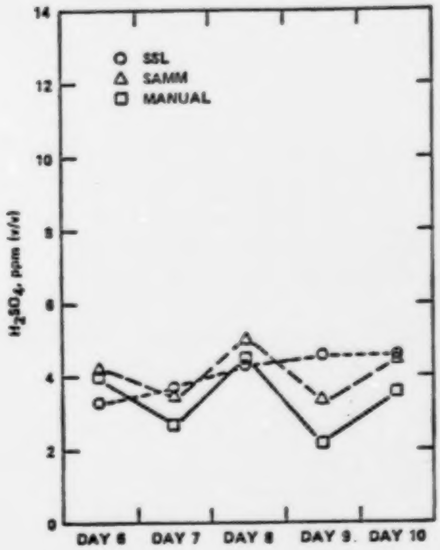


Figure 6-3. Comparative Studies: Outlet

This information was compiled from daily values. A typical daily compilation is shown in Figure 6-4.

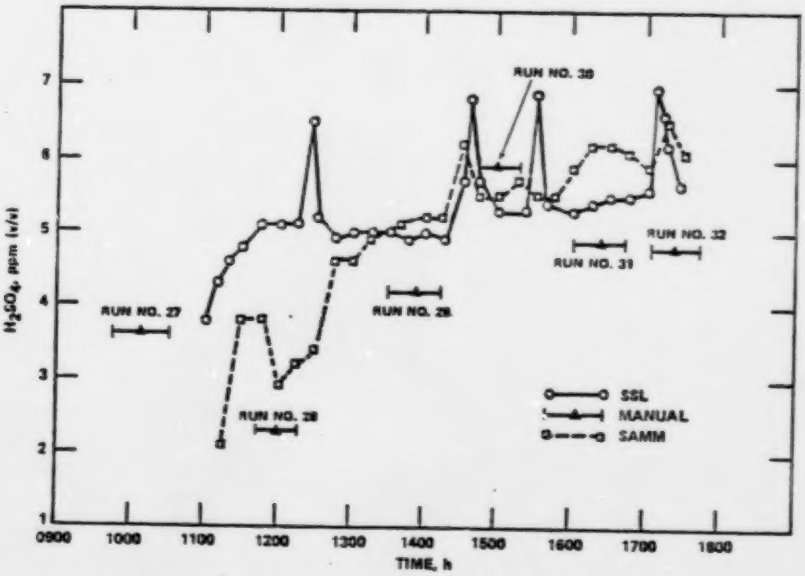


Figure 6-4. Comparative Study: Daily Compilation

Better agreement is found on the average than for individual data points.

6.1.4 Sulfuric Acid Mist Monitor/Federal Reference Method 8

Rockwell International,[143] under contract to EPA, evaluated the SAMM system for relative accuracy with EPA Federal Reference Method 8, which was designed to monitor SO_3/H_2SO_4 emissions from sulfuric acid plants. Field testing of this instrument was performed at a dual contact acid production plant equipped with a demister. The stack emissions were sampled simultaneously by the monitor and by Reference Method 8. Results of these tests are shown in Table 6-4 and Figure 6-5.

TABLE 6-4

COMPARATIVE STUDY: SULFURIC ACID MIST MONITOR AND FEDERAL REFERENCE METHOD 8

Sample No.	SO_2 (ppm)	H_2SO_4 (mg/m^3) Reference[1]	SAMM	% Error[2]
1	554	8.9	7.6	-14.6
2	564	7.4	7.4	-
3	569	4.6	5.8	+26.1
4	567	4.9	5.4	+10.2
5	564	5.2	6.0	+15.4

1 EPA Reference Method 8
2 Relative to Reference Method

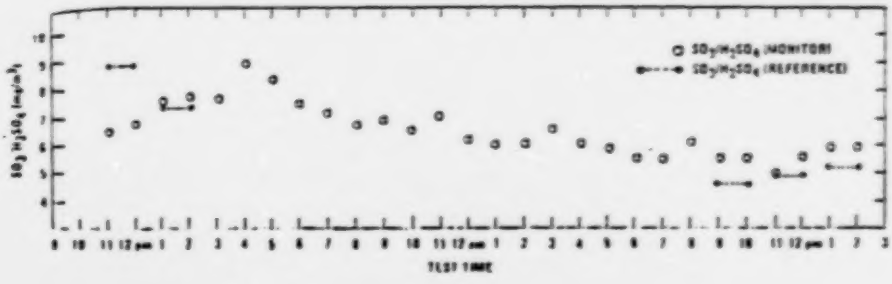


Figure 6-5. Comparative Study: Sulfuric Acid Mist Monitor and Federal Reference Method 8

6.1.5 Modified Federal Reference Method 6/Controlled Condensation System

Characterization studies were carried out by EPA at a 830 MW boiler unit firing low-grade sub-bituminous coal having a sulfur content of about 5%[144]. The SO_2 control system had a limestone scrubber equipped with demisters to remove entrained water droplets.

The sampling protocol used the controlled condensation system for sulfuric acid vapor measurements and the Modified Federal Reference Method 6 sampling train for total water solube sulfates (TWSS). Comparison samples were taken at both the inlet and the outlet of the limestone scrubber. A summary of the comparative measurements is given in Table 6-5.

TABLE 6-5

COMPARATIVE STUDY: MODIFIED FEDERAL REFERENCE METHOD 6 AND CONTROLLED CONDENSATION SYSTEM

Sample No.	Location	Sulfur Dioxide, ppm		Sulfates, ppm	
		Modified Method 6	Controlled Condensation System	Modified[1] Method 6	Controlled[2] Condensation System
1	Inlet	3845	3345	34.8	37.8
2	Outlet	1073	1138	62.1	44.9
3	Outlet	1552	1578	45.2	40.7
4	Outlet	1778	2095	43.6	52.3

1 Total sulfates = probe plug, probe wash, IPA impinger, impinger plug
2 Total sulfates = probe wash, filter wash, condenser catch + frit

The results indicate a good agreement between SO_2 values and total water soluble sulfate (TWSS) values. Table 6-6 indicates average values for outlet sampling for both the modified Method 6 and the controlled condensation system.

TABLE 6-6

COMPARATIVE STUDY: OUTLET

Sampling System	Average ppm/% of Total			
	PW/PW	PP/Filter	IPA/Cond.	IP/IPA
Modified Method 6	5/12	23/52	15/35	1/3
Controlled Condensation	3/8	3/17	10/54	1/6

PW = Probe wash, PP = probe plug (MM6); Filter = Filter (ccs); IPA = IPA impinger (MM6); Cond. = Condenser (ccs); IP = Impinger plug (MM6); IPA = IPA impinger (ccS).

The values indicate the difference in sulfate distribution between the two systems. In the Modified Method 6 train, the majority of the sulfate was found on the probe plug, even though the probe was maintained above the dew point of the acid.

7.0 SULFURIC ACID MONITORING SYSTEMS - ADVANTAGES AND DISADVANTAGES

The ability to monitor sulfuric acid from a combustion source is a difficult task. All monitoring techniques have inherent problems, and while a particular method may have the ability to distinguish between sulfuric acid and particulate sulfates, it may require considerable technical knowledge to obtain satisfactory results. On the other hand, another method may require minimum experience to operate, yet provide questionable results. It is, therefore, important for the user to understand the limitations and advantages of each monitoring method.

Table 7-1 discusses advantages and disadvantages and lists specific comments for each method.

TABLE 7-1
SULFURIC ACID MONITORING SYSTEMS: ADVANTAGES AND DISADVANTAGES

METHOD	ABBREVIATION	VARIABLE MEASURED	TIME REQUIRED	ADVANTAGES	DISADVANTAGES	COMMENTS
Deposition Rate Probe	(DRP)	Rate of acid deposition	3 to 5 hr. including set-up & lab work	o Can determine acid dew point & rate of acid deposition o Can run additional analysis	o Good analytical techniques needed o Particulate build-up causes interference o Warmup error	o Data scattered, hard to interpret o Distinct acid dew point hard to find o Limited number of data points can be taken
Dew Point Meter	(DPM)	Temperature at which acid condenses on probe. Rate of acid deposition	1/2-2 hr.	o Quick and easy o Measures rate of buildup (RBU) and dew point o Portable; (can go to many locations in one day)	o Dirty gas stream interferes o H_2SO_4 aerosol interferes Low acid concentration may require several hours to get dew point	o Calibration difficult o Reproducibility poor o No sample collected for further analysis
Controlled Condensation System	(CCS)	$SO_3/H_2SO_4/SO_2$ and other appropriate gases	1-2 hr.	o Direct measurement of sulfuric acid vapor o Sulfur balance can be determined	o Collection efficiency questionable o Temperature control critical o Flow rate critical o SO_2 oxidation may occur o Particulate/gas separation questionable o Complete sample recovery needed	o Bulky o Reproducibility problems o Long probe required o Recovery critical; laboratory techniques must be good
Modified Federal Reference Method 6	(MM6)	Total Water Soluble Sulfates (TWSS) & SO_2	1/2-2 hr.	o Compact, simple to operate o Limited experience to operate	o SO_2 oxidation may occur o Particulate/gas separation o Artifact formation o Metal interference	o Only gives TWSS & SO_2 values o Requires good laboratory technique

TABLE 7-1 (Continued)

SULFURIC ACID MONITORING SYSTEMS: ADVANTAGES AND DISADVANTAGES

METHOD	ABBREVIATION	VARIABLE MEASURED	TIME REQUIRED	ADVANTAGES	DISADVANTATES	COMMENTS
Severn Science Ltd. Continuous SO_3/H_2SO_4 Analyzer	(SSL)	SO_3/H_2SO_4	2 min.	o Portable, compact o Umbilical cord allows for flexibility, adapatability o Monitor simple to operate o Can visit many locations at one source	o Equilibrium time required o Artifact formation may occur o Solution reservoir needs periodic refills o Minimum moisture required for proper operation (>4%)	o Frequent adjustments of flow rates
Miniture acid condensation system	(MACS)	SO_3/H_2SO_4	1-2 hr.	o Transported/ reassembled with minimum of effort o One man operation o Can visit many locations at one source	o Limitation of sampling flow rate o If low sulfuric acid vapor, then long sampling time	o Much better than larger controlled condensation version o Not commercially available
Sulfuric acid mist monitor	(SAMM)	SO_3/H_2SO_4	1-999 sec.	o Monitors sulfuric acid vapor	o Must reach equilibrium o Mass flow controller problems o Refrigeration system fails often o Moisture needed in gas stream(>4%) o Bulky, heavy o Undetected leaks in gas sampling system may cause problems	o Satisfactory degree of reproducibility o Extreme care in handling because of glassware o Not commercially available

TABLE 7-1 (Continued)

SULFURIC ACID MONITORING SYSTEMS: ADVANTAGES AND DISADVANTAGES

METHOD	ABBREVIATION	VARIABLE MEASURED	TIME REQUIRED	ADVANTAGES	DISADVANTATES	COMMENTS
Federal Reference Method 8	(RM8)	$SO_3/H_2SO_4/SO_2$	1-2 hrs	o Reference Method for sulfuric acid plants	o Particulate interference o Metal interference o Isokinetic sampling required	o Laboratory techniques must be good o Bulky o Applicable to sulfuric acid plants only
Laser Analytics Tunable Diode Laser	(TDL)	H_2SO_4	Instantaneous	o Can distinguish between sulfuric acid and particulate o No particle/gas separation required	o Not a field instrument o High technical capability required to operate o In-situ monitor; therefore, can't move around easily	o Research tool o Expensive o Need high level of technical experience to operate
Remote Optical Sensing of Emissions	(ROSE)	H_2SO_4	Instantaneous	o Can distinquish between sulfuric acid and particulate o No particle/gas separation o Remote monitoring capability	o Field instrument, but a high level of technical background needed to operate	o Research tool o Expensive o Need technical experience to operate o Not commercially available

REFERENCES

1. H. F. Johnstone. "An Electrical Method for the Determination of the Dew Point of Flue Gases." Illinois University, Engineering Experiment Station, Cir. No. 20, 1929.

2. C. F. Goodeve. "Application of Filter Paper in the Determination of Sulfuric Acid Vapor in Boiler Flue Gas." Trans. Farraday Society, Vol. 32, p. 1218, 1936.

3. A. A. Taylor. "Relationship Between Dew Point and the Concentration of Sulfuric Acid in Flue Gas." J. Inst. Fuel, 16:25-28, 1942.

4. Knol, B. P., Paper 54, Central Technical Institute TNO, Delft.

5. D. Flint. "The Investigation of Dew Point & Related Condensation Phenomena in Flue Gases." J. Inst. Fuel, 1948, Vol. 21, p. 248.

6. P. F. Corbett. "A Phototurbidimetric Method for Estimation of SO_3 in the presence of SO_2." J. Soc. Chem. Ind. , 1948, Vol.. 67, p. 227.

7. P. F. Corbett. "The Determination of Sulfur Dioxide & Sulfur Trioxides." J. Inst. Fuel, 24:247-251, 1951.

8. Corbett, P. F., D. Flint & R. F. Littlejohn. "Development in the BCURA Dew Point Meter for the Measurement of the Rate of Acid Build-up on Cooled Surfaces Exposed to Flue Gases." J. Inst. Fuel, 25:246-258, 1952.

9. Muller, P. "Study of the Influence of Sulfuric Acid on the Dew Point Temperature of the Flue Gas." Chemie-Ing. - Tech, 1959, Vol. 31, p. 345.

10. Fielder, R. S., P. J. Jackson & E. Raask, "Determination of Sulfur Trioxide and Sulfur Dioxide in Flue Gases." J. Inst. Fuel, 33:84-92, 1960.

11. B. P. Knol. "Improvement in Determination of SO_3 and SO_2 in Combustion Gases." Riv. Combustible, 4, 542 (1960).

12. Goksoyr, H. and K. Ross. "The Determination of Sulfuric Trioxide in Flue Gases." J. Inst. Fuel, 35:177 (1962).

13. Clark, N. D. and G. D. Childs. "Boiler Flue-Gas Measurements Using a Dew Point Meter." ASME, Paper No. 63-WA-108, November, 1963.

14. Lisle, E. S. and J. D. Sensenbaugh. "The Determination of Sulfur Trioxide and Acid Dew Point in Flue Gases." Combustion, 1965, Vol. 36, No. 1, p. 12.

15. Environmental Protection Agency, "Standards of Performance for New Stationary Sources." Federal Register, Vol. 36, No. 247, pp 24876-24895, 1971.

16. Streiff, M. L. and C. B. Ludwig. "Remote Sensing of Air Pollution in Urban Areas." Final Report #EPA-650/2-73-026, August 1973.

17. American Society of Testing Materials, Part 26, ASTM Method D3226-73T, 1974.

18. Verhoff, F. H. and J. T. Banchero, "Predicting Dew Points of Flue Gases," Chemical Engineering Progress, Vol. 70, NO. 8, pp. 71-72, 1974.

19. Cheney, J. L., W. T. Winberry, and J. B. Homolya. "A Sampling and Analytical Method for the Measurement of Primary Sulfate Emissions." J. Environ. Sci. Health, 1977, Vol. A12, No. 10, p. 549.

20. Maddalone, R. F. and N. Garner. "Progress Measurements Procedures for Sulfuric Acid Emissions." TRW DSSG, EPA Contract #68-02-2165, Task No. 13, February 1977.

21. T. Land. "The Theory of Acid Deposition and Its Application to the Dew Point Meter." J. Inst. Fuel, Vol. 6, No. 77, p. 68.

22. Dietz, R. N., R. F. Wieser, and L. Newman. "Evaluation of a Modified Method of Flue Gas Sampling Procedure." Workshop Proceedings on Primary Sulfate Emissions from Combustion Sources, Volume 1: Measurement Technology, EPA 600/9-78-020a, August 1978.

23. Dietz, R. N., R. F. Wieser, and L. Newman. "An Evaluation of a Modified Method 6 Flue Gas Sampling Procedure." Workshop Proceedings on Measurement Technology and Characterization of Primary Sulfur Oxides Emissions from Combustion Sources," EPA 600/9-78-020b.

24. Pearson, E. F. and A. W. Mantz, "A Tunable Diode Laser Stack Monitor for Sulfuric Acid Vapor." EPA Contract 68-02-2990.

25. Jain, A. K., R. D. Blosser, and H. S. Oglesby. "Measurement of SO_3/H_2SO_4 Concentration in Kraft Recovery Furnace Stack Gas Using Controlled Condensation." Workshop Proceedings on Primary Sulfate Emissions from Combustion Sources, EPA 600/9-78-020a, August 1978.

26. Cheney, J. L. and W. Eaton, "The Construction and Preliminary Field Testing of a Prototype Sulfuric Acid Mist Monitor" Chem. Biomed. and Environ. Instrumentation, 1979, Vol. 9, No. 3, pp. 297-314.

27. Maddalone, R. F., S. F. Newton, R. G. Rhudy, and R. M. Statnick. "Laboratory and Field Evaluation of the Controlled Condensation System for SO_3 Measurements in Flue Gas Streams." J. Air Poll. Cont. Assoc., 1979, Vol. 29, p. 626.

28. Cheney, J. L., and J. B. Homolya. "Sampling Parameters for Sulfate Measurement and Characterization. "Environ. Sci. Technol., 1979, Vol. 13, p. 584.

29. Cheney, J. L., C. L. Walters, and J. B. Homolya. "Application of an Electrostatic Precipitator for Instrumental Sampling of Sulfuric Acid." Anal. letters, 1979, Vol. 12, No. A7, pp. 783-801.

30. Herget, W. F. and J. D. Brasher. "Remote Fourier Transform Infrared Air Pollution Studies," Optical Engineering, 1980, Vol. 19, No. 4, p. 508-514.

31. Jackson, P. J., D. A. Hilton, and J. H. Buddery. "Continuous Measurement of Sulfuric Acid Vapor in Combustion Gases Using a Portable Automatic Monitor." J. Int. Fuel, 1981, Vol. 27, p. 124.

32. W. R. Dickson. "Comparison of Automated and Manual Sulfuric Acid Sampling Systems." Southern Research Institute, EPA Contract 68-02-3461, April 1982.

33. Doyle, B. W. and Richard C. Booth. "Some Recent Data on SO_3 and SO_4 Levels in Utility Boilers." Workshop Proceedings on Primary Sulfate Emissions from Combustion Sources, EPA 600/9-78-020b.

34. Dooley, A. and G. Whittingham. "The Oxidation of Sulfur Dioxide in Gas Flames." J. Inst. Fuel, 1945, Vol. 18, p. 25.

35. Cullis, C. F. and M. F. R. Mulcahy. "The Kinetics of Gaseous Sulfur Compounds, Combustion and Flame." 1972, Vol. 18, p. 225.

36. Merryman, E. L. and A. Levy. Sulfur Trioxide Flame Chemistry - H_2S and CDS Flames Thirteenth (International) Combustion Symposium, The Combustion Institute, 1971, p. 427.

37. Robinson, E. and R. C. Robbins. Source Abundance and Fate of Gaseous Atmospheric Pollutants, Sanford Research Institute Project PR 6735, February 1968.

38. Levy, A. J., F. Kircher, and E. L. Merryman. "Effects of Combustion Modification on SO_3 Formation in Combustion." Workshop Proceedings on Primary Sulfate Emissions from Combustion Sources, EPA 600/9-78-020b, 1978.

39. Levy, A. J., F. Kirchen, and E. L. Merryman, Ibid.

40. Hillenbrand, L. J., R. G. Engdahl, and R. E. Barrett, Chemical Composition of Particulate Air Pollutants From Fossil-Fuel Combustion Sources, Battelle Columbus Laboratories, P. II-2, March 1, 1973.

41. Abel, E. "The Vapor Phase above the System Sulfuric Acid-Water." J. Phys. Chem., 1946, Vol. 50, p. 260.

42. P. Muller, Ibid.

43. Banchero, J. T. and F. H. Verhoff, Ibid.

44. Alexander, P. A., R. S. Fielder, P. J. Jackson and E. Raashk. "An Air Cooled Probe for Measuring Acid Deposition in Boiler Flue Gases," Journal of the Institute of Fuels, Vol. 33, 1960, pp 31-37.

45. Corbett, P. F., D. Flint and R. F. Littlejohn, *Ibid*.

46. D. Flint. *Ibid*.

47. Cheney, J. L., W. T. Winberry, and J. B. Homolya. *Ibid*.

48. Dietz, R. N., R. F. Wieser, and L. Newman. *Ibid*.

49. B. P. Knol. Paper 54, Central Technical Institute TNO, Delft.

50. Goksoyr, H. and K. Ross. *Ibid*.

51. Dietz, R. N., R. F. Wieser, and L. Newman. *Ibid*.

52. Cheney, J. L., and J. B. Homolya. *Ibid*.

53. Maddalone, R. F., S. F. Newton, R. G. Rhudy, and R. M. Statnick. "Laboratory and Field Evaluation of the Controlled Condensation System for SO_3 Measurements in Flue Gas Streams." *J. Air Poll. Centr. Assoc.*, 1979, Vol. 29, p. 622.

54. R. F. Maddalone. "Guideline for Combustion Source Sulfuric Acid Emission Measurements." EPA Contract #68-02-2165, Task Order No. 13.

55. Brooks, E. F., and R. L. Williams. "Process Stream Volumetric Flow Measurement and Gas Sample Extraction Methodology." TRW Defense and Space Systems, EPA Contract 68-02-1412, Task 13.

56. J. L. Cheney. "Miniature Acid Condensation System (MACS): System/Operational Manual." EPA, ESRL, RTP, N.C. Unpublished.

57. Cheney, J. L. and W. Eaton. *Ibid*.

58. Knight, B. A., E. F. Brooks, and R. F. Maddalone. "Development of an Automatic H_2SO_4 Monitor," EPA 600/7-79-153.

59. Jackson, P. J., D. A. Hilton, and J. H. Buddery. "Continuous Measurement of Sulfuric Acid Vapour in Combustion Gases Using a Portable Automatic Monitor." *J. Int. Fuel*, 1981, Vol. 27, p. 124.

60. W. F. Herget. "Remote and Cross-Stack Measurement of Stack Gas Concentration Using a Mobile FT-IR System." Applied Optics, 1982, Vol. 21(4), p. 635.

61. Pearson, E. F. and A. W. Mantz, "A Tunable Diode Laser Stack Monitor for Sulfuric Acid Vapor." EPA Contract 68-02-2990.

62. H. F. Johnstone. *Ibid*.

63. E. Abel. *Ibid*.

64. C. H. Greenewalt. "Partial Pressure of Water Out of Aqueous Solutions of Sulfuric Acid." *Ind. and Eng. Chem*. Vol. 17, pp. 522-523.

65. Gmitro, J. I. and T. Vermuelon. "Vapor-Liquid Equilibria for Aqueous Sulfuric Acid." Univ. of Calif. Radiation Lab. Report 10866, Berkeley, Cal., June 24, 1963.

66. Lisle, E. S. and J. D. Sensenbaugh. Ibid.

67. P. Muller. Ibid.

68. A. A. Taylor. "Relation Between Dew Point and the Concentration of Sulfuric Acid in Flue Gases." J. Inst. Fuel, 1942, Vol. 16, p. 25.

69. Gibson, G. and B. Kufta. "Cold-End Corrosion Monitoring Methods." Power Engineering, Vol. 81, No. 4, pp. 70-73.

70. T. Land. Ibid.

71. T. Land. Ibid.

72. M. O. Amdur. "Toxicologic Appraisal of Particulate Matter, Oxides of Sulfur and Sulfuric Acid." J. Air Poll. Control Association, 1969, Vol. 19, p. 638.

73. M. O. Amdur. "The Impact of Air Pollutants on Physiological Responses of the Respiratory Tract." Proc. Am. Phil.Soc., 1970, Vol. 114, No. 1, p. 3.

74. F. E. Speizer. "An Epidemiological Appraisal of the Effects of Ambient Air on Health: Particulates and Oxides of Sulfur." J. Air. Poll. Control Assoc., 1969, Vol. 19, p. 647.

75. J. Firket. "Fog Along the Meuse Valley." Trans. Faraday Soc., 1936, Vol. 32, p. 1192.

76. Schrenk, H., H. Heimann, G. D. Clayton, W. M. Gaffaffer, and H. Wexler. "Air Pollution in Donora, Pa.: Epidemiology of the Unusual Smog Episode of October, 1948." U.S. Publ. Health Bull. No. 306, 1949.

77. Greenburg, L., M. B. Jacobs, B. M. Rolette, F. Field, and M. M. Baverman. "Report of Air Pollution Incident in New York City, November, 1963." Publ. Hlth. Reports, 1962. Vol. 77, p. 7.

78. Homolya, J. B. and J. L. Cheney. "A Study of the Local Ambient Air Impact of Primary Sulfate Emission from the Combustion of Residual Oil." 175th Annual ACS Meeting, Anaheim, California, March 1978.

79. Homolya, J. B., H. M. Barnes, and C. R. Fortune. "A Characterization of Gaseous Sulfur Emissions from Coal and Oil-fired Boilers." Proceedings of the Fourth National Conference on Energy and the Environment, pp. 490-494, October 1976.

80. Hamill, H. F., R. E. Thomas, and D. Comann. "Collaborative Study of Methods for the Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources." Southwest Research Institute, NTIS PB-240-752/6, November 1974.

81. Hamill, H. F., R. E. Thomas, and D. Comann. Ibid.

81. W. T. Winberry. "SO_2 Oxidation in 80% Isopropanol Solution." Unpublished data.

82. W. T. Winberry. "Source Sampling and Analysis of Gaseous Pollutants." Air Pollution Training Institute, Course Manual 468, EPA 450/2-81-009, May 1981.

83. Jain, A. K., R. O. Blosser, D. B. Newport, and H. S. Oglesby. "Evaluation and Application of SO_x Measurement Procedures for Kraft Recovery Furnaces." NTIS PB-81-109092.

84. P. F. Corbett. "A Phototurbidimetric Method for Estimation of SO_3 in the presence of SO_2." J. Soc. Chem. Ind., 1948, Vol. 67, p. 227.

85. D. Flint. "Determination of Small Concentrations of SO_3 in the Presence of Larger Concentrations of SO_2." J. Soc. Chem. Ind., 1948, Vol. 67, No. 2, p. 2.

86. Fielder, R. S., P. J. Jackson, and E. Raask. "Determination of SO_2 and SO_2 in Flue Gases." J. Inst. Fuel, 1960, Vol. 33, p. 84.

87. Seidman, E. B. "Determination of Sulfur Oxides in Stack Gases." Anal. Chem., 1958, Vol. 30, p. 1680.

88. Fielder, R. S. and Morgan, C. H. "An Improved Titrimetric Method for Determining Sulfur Trioxide in Flue Gas." Anal. Chem. Acta, 1960, Vol. 23, p. 538.

89. Cheney, J. L., W. T. Winberry, Jr., and J. B. Homolya. Ibid.

90. Dietz, R. N., R. F. Wieser, and L. Newman. "An Evaluation of a Modified Method 6 Flue Gas Sampling Procedure." Workshop Proceedings on Measurement Technology and Characterization of Primary Sulfur Oxides Emissions from Combustion Sources," EPA 600/9-78-020b.

91. Dietz, R. N., R, F, Wieser, and L. Newman. "Evaluation of a Modified Method of Flue Gas Sampling Procedure." Workshop Proceedings on Primary Sulfate Emissions from Combustion Sources, Volume 1: Measurement Technology, EPA 600/9-78-020a, August 1978.

92. W. T. Winberry. "SO_2 Oxidation in 80% Isopropanol Solution," unpublished data.

93. Cheney, J. L., W. T. Winberry, and J. B. Homolya. Ibid.

94. Dietz, R. N., and R. F.Wiesser. "Sulfate Emissions from Fossil Fuel Combustion Sources." Brookhaven National Laboratory, Progress Report No. 5, September 1977.

95. Dietz, R. N. and R. F. Wieser. "Power Plant Flue Gas and Plume Sampling Studies." Brookhaven National Laboratory, Progress Report No. 2, December 1978.

96. Knoll, J. E. and M. R. Midgett. "An Evaluation Study of EPA Method 5," EPA-600/4-80-018, March, 1960.

97. Cheney, J. L., W. T. Winberry, and J. B. Homolya. Ibid.

98. McCurley, W. R., and D. G. DeAngelis. "Measurement of Sulfur Oxides from Coal-Fired Utility and Industrial Boilers." Workshop Proceedings on Measurement Technology and Characterization of Primary Sulfur Oxides Emissions from Combustion Sources, EPA 600/9-78-020b.

99. Maddalone, R. F., S. F. Newton, R. G. Rhudy, and R. M. Statnick. "Laboratory and Field Evaluation of the Controlled Condensation System for SO_3 Measurements in Flue Gas Streams." J. Air Poll. Cont. Assoc., 1979, Vol. 29, p. 626.

100. Cheney, J. L. and J. B. Homolya. Ibid.

101. Dietz, R. N., R. F. Wieser, and L. Newman. Ibid.

102. Cheney, J. L., C. L. Walters, and J. B. Homolya. "Application of an Electrostatic Precipitator for Instrumental Sampling of Sulfuric Acid." Anal. Letters, 1979, Vol. 12, No. A7, pp. 783-801.

103. Jain, A. K., R. D. Blosser, and H. S. Oglesby. "Measurement of SO_3/H_2SO_4 Concentration in Kraft Recovery Furnace Stack Gas Using Controlled Condensation." Workshop Proceedings on Primary Sulfate Emissions from Combustion Sources, EPA 600/9-78-020a, August 1978.

104. Cheney, J. L. and J. B. Homolya. Ibid.

105. Peters, E. T. and J. W. Adams. "Sulfur Oxide Interaction with Filters Used for Method 5 Stack Sampling." Workshop Proceedings on Primary Sulfate Emissions from Combustion Sources, EPA 600/9-78-020a, August 1978.

106. Maddalone, R. F., S. F. Newton, R. G. Rhudy, and R. M. Statnick. Ibid.

107. Lundgren, D. A. and T. C. Gunderson. "Filtration Characteristics of Glass Fiber Filter Media at Elevated Temperatures." EPA 600/2-76-192, July 1976.

108. W. J. Mitchell. "Summary Test Report; Comparative Evaluation of EPA Methods 5 and 17, Miami Fort Power Plant, Cincinnati, Ohio." PEDCo Environmental, EPA Contract 68-02-3431, Task Nos. 88 and 104, November 1981.

109. Jain, A. K., R. D. Blosser, D. B. Newport, and H. S. Oglesby. Ibid.

110. Jain, A. K., R. D. Blosser, D. B. Newport, and H. S. Oglesby. Ibid.

111. Peters, E. T. and J. W. Adams. Ibid.

112. Peters, E. T. and J. W. Adams. Ibid.

113. Gilman, C., and J. C. Marshall. High Purity Fibrous Air Sampling Media. Amer. Ind. Hyg. Assoc. Jour., 1975, Vol. 36, pp 512-517.

114. Maddalone, R. N., S. F. Newton, R. G. Rhudy, and R. M. Statnick. Ibid.

115. Jain, A. K., R. D. Blosser, and H. S. Oglesby. Ibid.

116. Cheney, J. L. and J. B. Homolya. Ibid.

117. W. J. Mitchell. "Summary Test Report: Comparative Evaluation of EPA Method 5 and 17," US EPA, Contract No. 68-02-3431, November 1981.

118. Dietz, R. N. and R. F. Wiesser. Ibid.

119. Cheney, J. L., C. L. Walters, and J. B. Homolya. Ibid.

120. P. Drinker. J. Indust. Hyg., 1932, Vol. 14, No. 10, p. 364.

121. Cheney, J. L., C. L. Walters, and J. B. Homolya. Ibid.

122. Jain, A. K., R. D. Blosser, and H. S. Oglesby. Ibid.

123. Dietz, R. N. and R. F. Wiesser. Ibid.

124. Cheney, J. L. and J. B. Homolya. Ibid.

125. Maddalone, R. F., S. F. Newton, R. G. Rhudy, and R. M. Statnick. Ibid.

126. Jain, A. K., R. D. Blosser, and H. S. Oglesby. Ibid.

127. Maddalone, R. F., S. F. Newton, R. G. Rhudy, and R. M. Statnick. Ibid.

128. Lisle, E. S. and J. D. Sensenbaugh. Ibid.

129 Perry's Chemical Engineers' Handbook. McGraw-HIll Book Company, 4th Edition, p. 59.

130. Cheney, J. L. and J. B. Homolya. Ibid.

131. Winberry, W. T. and B. Dellinger. "Investigation Into the Frit Plugging of the Goksoyr/Ross Coil." Northrop Services Inc., EPA Contract 68-02-2566, T.D. 3.3-31.

132. Winberry, W. T. and B. Dellinger. Ibid.

133. Cheney, J. L. and J. B. Homolya. Ibid.

134. Cheney, J. L., J. B. Homolya, and H. M. Barnes. "A Comparison of Three Combustion Source Sulfate Emissions Characterization Methods." AICHE, Symposium Series, 1979, Vol. 75, p. 188.

135. Hunter, S. C. and N. L. Helgeson. "Control of Oxides of Sulfur from Stationary Sources in the South Coast Air Basin of California." NTIS No. PB-261-754, June 1975.

136. G. A. Cato. "Field Testing Application of Combustion Modifications to Control Pollutant Emissions from Industrial Boilers - Phase II." EPA 600/2-76-086a, NTIS PB-253-500, April 1976.

137. G. A. Cato. "Field Testing: Trace Element and Organic Emissions from Industrial Boilers." EPA 600/2-76-086b, October 1976.

138. KVB, Inc. Data Obtained from Industrial and Utility Client Program, 1970-1977.

139. P. K. Engel. "Diesel Exhaust Fouling and Corrosion Evaluation Program, Task II, Diesel Exhaust Analysis." Final Report, KVB 21803-775, April 1978.

140. K. L. Maloney. "Systems Evaluation of the Use of Low-Sulfur Western Coal in Existing Small and Intermediate-Size Boilers." EPA Contract 68-02-1863, Draft Report Submitted to EPA.

141. P. K. Engel. Ibid.

142. W. R. Dickson. "Comparison of Automated and Manual Sulfuric Acid Sampling Systems." Southern Research Institute, EPA Contract 68-02-3461, April 1982.

143. Cheney, J. L. and W. Eaton. Ibid.

144. W. T. Winberry, Jr.. "Kansas City Power & Light Company - Cumulative Data." Northrop Services Inc., EPA Contract 68-02-2566, T.D. 3.3-26.

APPENDIX A

SULFURIC ACID AEROSOL GENERATOR

APPENDIX A

SULFURIC ACID AEROSOL GENERATOR

1.0 INTRODUCTION

The main requirement for evaluating any analytical method is the availability of primary standards. The standards not only must contain known amounts of the species of interest, but also they must duplicate the sample matrix in which that species is found. The use of standards meeting these requirements, provides a reasonable degree of confidence in the sampling systems to which the standards are applied.

The increased interest in sulfuric acid emissions from combustion sources has warranted the development of sulfuric acid monitors. With their development has come a concurrent need to provide some form of validation of the monitor by the use of a stable source of sulfuric acid mist. Because of the characteristics of source emissions, the generator should be able to provide a concentration from 0 g/min to 3 mg/min in a total flow of 1 to 15 l/min. In addition, the generator should be able to provide source level matrix pollutants (SO_2, CO_2, CO, and H_2O) for stable and reproducible periods of several days.

Historically, researchers[1-6] have developed numerous techniques for generating sulfuric acid mist at ambient levels for health effects studies. These techniques range from nebulization of dilute sulfuric acid solutions to atomizer-burner techniques. Such procedures have now been applied to generating source level sulfuric acid aerosols. Techniques range from fuming sulfuric acid to the more modern thermal oxidation of SO_2 to produce sulfuric acid aerosol. Table 1-1 lists those techniques most commonly associated with source level sulfuric acid generators.

TABLE 1-1

TECHNIQUES FOR GENERATING SULFURIC ACID AEROSOL

Investigator	Method	H_2SO_4 Mass Rate, mg/min	H_2SO_4 Concentration, ppm	Repeatability	Problems
Carabine & Maddock[7]	Nebulizing & Evaporating Sulfuric Acid Solutions	0.05-1	2-25	± 12%	o Inadequate mass balance
Dietz and Wiesen[8]	Sulfur Trioxide Permeation Tube	0.003-0.15	0.02-73	± 1%	o Temperature aging and conditioning effects o permeation tubes
Walters & Cheney[9]	Catalytic Oxidation of SO_2	0-0.08	0-21	± 1%	o Time needed (30 min) to reach equilibrium between changing sulfuric acid concentration
Cheney & Fortune[10]	Fuming Sulfuric Acid and Water Flask	0.1-2	0-98	± 5%	o Considerable time needed to reach equilibrium
Lisle & Sensenbaugh[11]	Evaporating Sulfuric Acid Solution	0.1-1	5-49	± 5%	o Inconsistent mass rates o Poor mass balance
Maddalone, Newton, Rhudy & Statnick[12]	Evaporating Sulfuric Acid Solution	0.1-1	5-49	± 7%	o Pulsing of syringe causes pulsing of sulfuric acid concentration within generator
Dickson[13]	Nebulizing & Evaporating Sulfuric Acid Solutions	0-2.2	2-20	± 5%	o Small H_2SO_4 concentration accomplished by varying air flow, but large changes in concentration require strength of solution change

Historically, many problems have been associated with the production of an accurate and stable sulfuric acid gas stream. These problems involve, but are not limited to, consistent moisture production, rate of aerosol growth and stability of the generator after changing conditions.

2.0 SULFURIC ACID AEROSOL GENERATORS

2.1 Fuming Sulfuric Acid Aerosol Generator

Cheney and Fortune developed one of the early source level sulfuric acid generators. Their effort combined the work of Scaringelli and Rehme[14] with that of Taylor[15] to produce a generator that duplicates sulfuric acid and moisture levels found in flue gases. The generator, shown in Figure 2-1, consists of four major components: (1) clean air supply, (2)mass flow meters, (3) reaction flask containing water and fuming sulfuric acid, respectively, and (4) heated quartz tube.

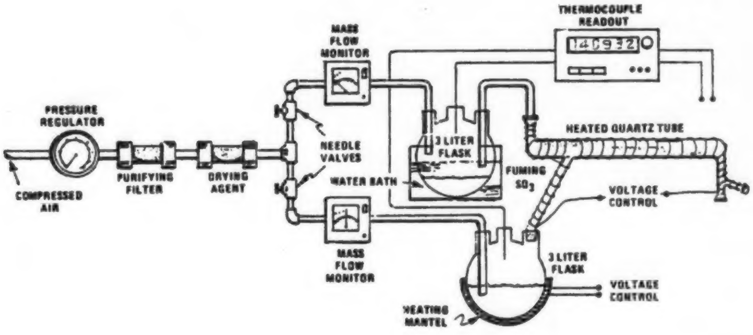


Figure 2-1. Fuming Sulfuric Acid Generator

The concentration of sulfuric acid produced is determined by proper temperature control of the fuming sulfuric acid flask and the flow ratios of the two make-up air streams. Moisture concentration is determined by monitoring the temperature of the air space above the heated water reservoir and calculating the percent moisture in the air stream through saturated vapor pressure tables.

Air used in the generator is purified, dried, and monitored by two mass flow meters. The production of sulfuric acid vapor and moisture is accomplished by passing the purified air over each temperature-controlled reservoir. By carefully controlling the temperatures of the acid and water reservoirs, as well as accurately monitoring the flow of the two streams, precise and repeatable concentrations of sulfuric acid mist and water vapor are attained. The two streams are combined in the heated quartz tube maintained between 260° and 315°C. Sampling of the exhaust gas stream by a sulfuric acid mist monitor is accomplished by attaching the monitoring system to the outlet of the heated quartz tube.

The acid generator was found to be a very predictable and repeatable system. The ability to reproduce the desired conditions is shown in Table 2-1.

TABLE 2-1

REPRODUCIBILITY OF GASEOUS SULFURIC ACID AEROSOL GENERATOR

Run	Air Flow[a] Water Flask	Air Flow[a] SO_3 Flask	Temp (°C) Water Flask	H_2SO_4[b]	%H_2O[c]
1	3900	100	43	23.2	9.2
2	3900	100	43	20.2	9.2
3	3900	100	43	22.5	9.4
4	3900	100	43	21.8	9.6
5	3750	250	43	62.2	7.8
6	3750	250	43	60.0	7.7
7	3750	250	43	58.9	7.8
8	3800	200	46	51.9	10.6
9	3800	200	46	48.5	10.6

[a] Air flow in cc/min, [b] H_2SO_4 in vol/vol as determined by barium-thorin titration, [c] %H_2O by EPA Reference Method 4

2.2 Permeation Tube Sulfuric Acid Aerosol Generator

Dietz and Wieser[16] recently developed a sulfuric acid generator utilizing the permeation tube technique developed by O'Keeffe.[17] The permeation tube method is based on the theory that a gas confined above its liquified form, at a constant temperature, will permeate through some material at a constant rate. The permeation of the vapor through the tube will take place because of the concentration gradient that exists between the inner and outer tube walls. By passing different flows of diluent gas over the tube, gases of varying concentrations can be generated. Figure 2-2 demonstrates a standard permeation tube used in the production of sulfuric acid aerosol.

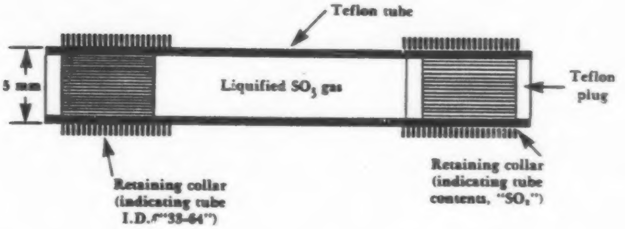

Teflon tube
5 mm
Liquified SO3 gas
Teflon plug
Retaining collar (indicating tube I.D.,"33-64")
Retaining collar (indicating tube contents, "SO3")

Figure 2-2. Standard Permeation Tube

The standard permeation tube is prepared by placing liquefied SO_3 in one end of a 0.25 in. copolymer tube sealed with a glass bead. The tube is then sealed at the other end and allowed to equilibrate at constant temperature and zero humidity for four days. A permeation rate is calibrated by determining the weight loss of the tube over an extended period of time (Figure 2-3); permeation rate is routinely reported in mg/cm/min. Permeation tubes can be constructed of either thin-walled or thick-walled material, and both perform well as shown in Figure 2-3.

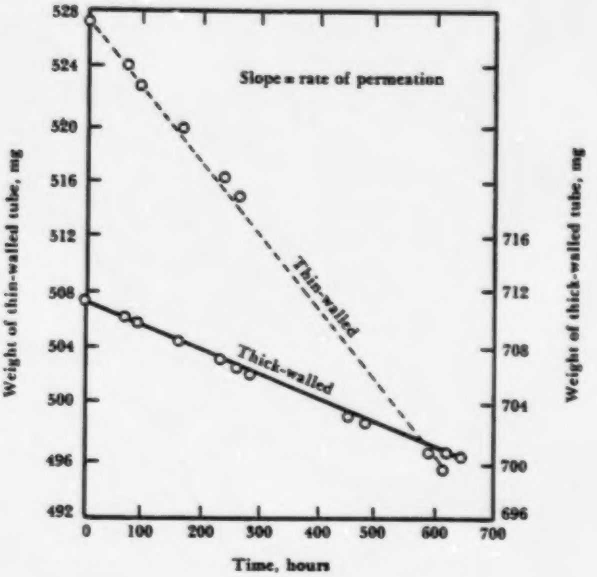


Figure 2-3. Calibration of Permeation Tubes

The sulfuric acid generator developed by Dietz and Wieser (Figure 2-4) consisted of constant temperature bath, a permeation tube for generating SO_3, a source of carrier gas to pass over the permeation tube, and an impinger system for detecting the concentration of SO_3 generated. By varying the flow rate over the tube, different levels of sulfuric acid aerosol can be generated. The dynamic range of the SO_3 generator is 0 to 75 ppm.

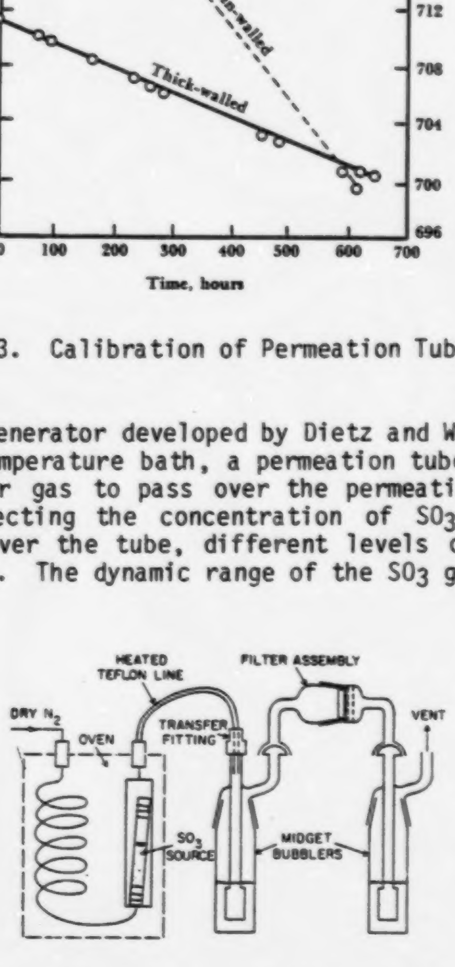


Figure 2-4. Dietz and Wieser Sulfuric Acid Aersol Generator

Table 2-2 indicates the long-term performance of the Dietz and Wieser permeation tubes, and Table 2-3 indicates the stability of the permeation tube sulfuric acid generator.

TABLE 2-2

LONG-TERM PERFORMANCE OF SO_3 PERMEATION TUBES

Date	Days in Service	No. of Runs	Avg. Temperature, °C	SO_3 permeation rate, equiv/h Measured	Calculated[a]
2/23/78	2	3	71.9 ± 1.3	101.9 ± 8.0	96.4 ± 8.2
1/29/79	342	3	56.0 ± 0.1	28.7 ± 0.4	29.0 ± 2.5

[a] Determined from $\ln P = 29.451 - (8587/T)K$

TABLE 2-3

STABILITY OF SO_3 PERMEATION TUBE SULFURIC ACID GENERATOR

Hours in Service	H_2SO_4 Titrated, equiv				Permeation rate, equiv/hour
	Bubbler 1	Filter	Bubbler 2	Total	
18	5.2	6.8	0.0	12.0	24.0
19	4.6	7.4	0.0	12.0	24.0
43	4.7	7.8	0.0	12.5	25.0
45	5.3	6.8	0.0	12.1	24.2
67	4.8	7.8	0.0	12.6	25.2
143	5.2	7.0	0.1	12.3	24.6
164	5.2	7.7	0.0	12.9	25.8
165	4.3	7.8	0.0	12.1	24.2
190	4.8	7.5	0.0	12.3	24.6
191	5.9	6.2	0.0	12.1	24.2

Average permeation rate = 24.6 ± 0.6 equiv/hour

2.3 Catalaytic Oxidation Sulfuric Acid Aerosol Generator

Concurrent with the development of the SO_3 permeation tube, Walter and Cheney designed and developed a high temperature sulfuric acid generator featuring the catalytic conversion of SO_2 to SO_3. This technique was pioneered by Wickert[19] in 1967.

The high-temperature sulfuric acid generator, as shown in Figure 2-5, consists of three major components: (1) the catalytic reaction chamber, (2) the mixing chamber, and (3) the humidity source.

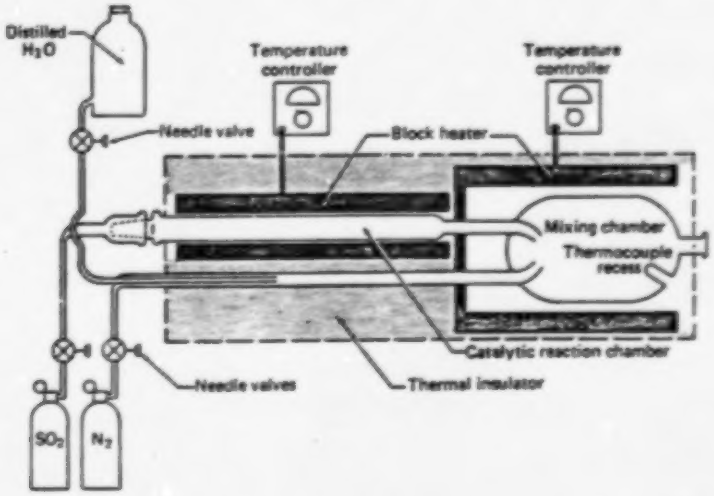


Figure 2-5. Catalytic Oxidation Sulfuric Acid Aerosol Generator

In operation, moisture is generated by direct injection of distilled water from a constant head volume bed into the heated carrier gas stream of nitrogen. Sulfur dioxide is provided to the catalytic reaction chamber from a compressed gas mixture of 1% SO_2 in air. The catalytic reaction chamber consists of a variably heated (20°C-538°C) quartz tube packed with platinum black dispersed on quartz wool by controlling the temperature of the converter, varying acid production can be cobtained. The SO_2 reacts with O_2 in the air on the platinum black catalyst to form SO_3. The SO_3 then passes into a heated mixing chamber where it combines with the controlled water vapor contained in the carrier gas to form sulfuric acid mist. Samples from the generator are taken at the outlet of the mixing chamber. The generator is designed to provide a gas concentration of 0-21 ppm of H_2SO_4 at flow rates of 1-20 l/min and outlet gas temperatures of 120°C to 290°C.

Walters and Cheney report acid production consistent at fixed operational parameter settings; when these parameters are changed and then reset to the original points, the acid concentration stabilizes at the previous level. Likewise, the generator is capable of providing a constant high temperature, high output volume of sulfuric acid in the presence of SO_2. Table 2-4 indicates the results of an extended operational test of the generator.

TABLE 2-4
EXTENDED OPERATION OF THE CATALYTIC OXIDATION SULFURIC ACID AEROSOL GENERATOR

Run #	% Moisture	Converter Temp. (°C)	Sulfuric Acid Aerosol Generator ppm	Sulfuric Acid Aerosol Generator $g/m^3 \times 10^4$	SO_2 ppm	Avg. % Conversion
1-6	11.0	538	20.2	8.22	ND	100
8-14	11.0	427	18.3	7.04	4.12	86.1
15-20	11.8	371	5.4	2.22	16.7	33.0
21-27	8.7	427	15.7	6.6	4.3	85.5

2.4 Nebulization Sulfuric Acid Aerosol Generator

Another common technique used to generate sulfuric acid mist is through nebulization of standardized sulfuric acid solutions into a sampling chamber. Dickson[20] utilized this approach in his study involving comparisons of automated and manual sulfuric acid sampling systems. In addition, the National Council of the Paper Industry for Air and Stream Improvement[21] has also used this approach in evaluating sulfur oxides measurement procedures for Kraft recovery furnaces.

The generator, shown in Figure 2-6, consists of a combination humidifier/air heater to provide proper moisture concentration, a nebulizer for producing an aerosol of sulfuric acid, and a heated quartz tube as the reaction/sampling chamber.

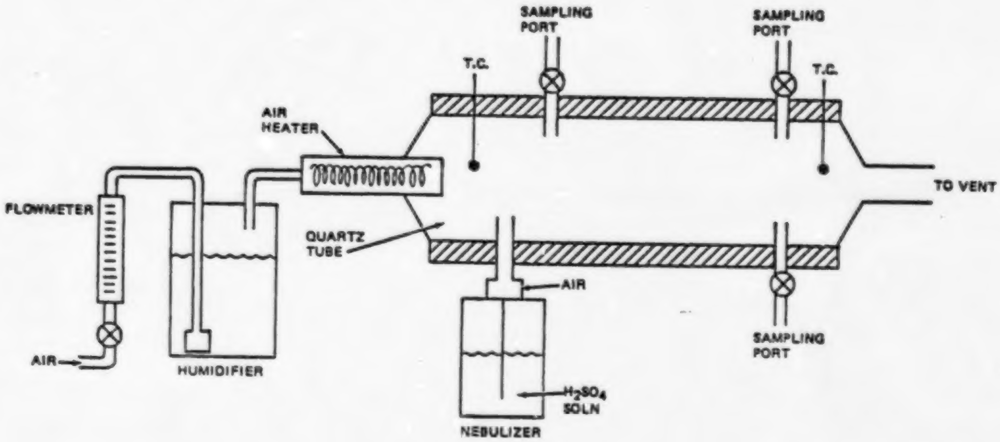


Figure 2-6. Nebulization Sulfuric Acid Aerosol Generator

The generation of sulfuric acid begins with clean air entering the humidifier at 300°C and passing through the air heater where it exits at about 280°C. This gas stream represents the temperature and moisture levels normally found at source emission levels. The production of sulfuric acid aerosol is accomplished as the air stream entering the nebulizer and forces sulfuric acid aerosol into the heated reaction/sampling chamber. Once in the chamber, it combines with the heated moisture stream to produce a standard sulfuric acid aerosol stream. Changes in the concentration of sulfuric acid aerosol produced can be obtained by either varying the air flow rate through the nebulizer or changing the concentration of the sulfuric acid solution. Sampling of the standardized gas stream is accomplished through sampling ports located at the end of the chamber.

The authors indicate that the generator can produce a stable gas stream of sulfuric acid vapor from 2 to 20 ppm with an average Relative Standard Deviation (RSD) of less than 5% at the 10 to 20 ppm level and less than 10% at the 2 to 4 ppm level.

2.5 Syringe/Evaporation Sulfuric Acid Aerosol Generator

A final approach to generating sulfuric acid vapor has been based on the design of Lisle and Sensenbaugh[22] to provide test gas streams of varying H_2SO_4, H_2O, SO_2, O_2, and N_2. This approach, utilized by Maddalone[23] in his evaluation of the controlled condensation system, consists of a syringe pump; a heated evaporator; a gas port to provide varying concentrations of O_2, SO_2, and N_2; and a sampling port for sampling test atmospheres (Figure 2-7).

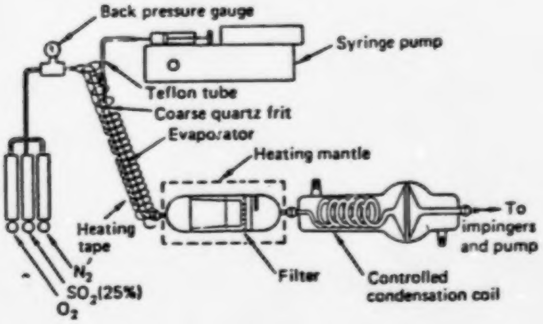


Figure 2-7. Syringe/Evaporation Sulfuric Acid Aerosol Generator

Different sulfuric acid vapor concentrations are generated by introducing H_2SO_4 solution into the evaporator by means of a syringe pump. Adjusting the H_2SO_4 solution strength and flow produces a range of sulfuric acid and moisture concentrations. Actual stack concentrations of SO_2, O_2, and N_2 are duplicated in the generator by selecting proper gas cylinder concentrations.

Laboratory evaluation found the sulfuric acid generator able to produce SO_3, H_2O, and H_2SO_4 concentrations that were 95 ± 6% reproducible.

REFERENCES

1. Chang, D. P. and B. K. Tarkington. J. Am. Ind. Hyg. Assoc., 1977, Vol. 38, pp. 493-497.

2. Chang, D. P. and B. K. Tarkington. J. Air Pollut. Control Assoc., 1978, Vol. 28, pp. 1137-1139.

3. Gillespie, G. R. and H. F. Johnstone. Chem. Eng. Prog, 1955, Vol. 51, pp. 74F-80F.

4. Cavender, F. L., J. L. Williams, W. H. Steinhagen, and D. J. Woods. Toxicol. Environ. Health, 1977, Vol. 2, pp. 1147-1159.

5. Thomas, R. L. and V. Dharmarajan. Environ. Sci. Technology, 1974, Vol.8, pp. 930-935.

6. Snyder, R. E., M. E. Tonkin and A. M. McKissick. "Evaluation of Methodology and Prototype To Measure Atmospheric Sulfuric Acid," EPA 600/2-79-168.

7. Carabine, M. D. and J. E. Maddock. Atmos. Environ, 1976, Vol. 10, pp. 735-742.

8. Dietz, R. N. and R. F. Wieser. "Sulfur Trioxide Permeation Tube for Calibration of Sulfuric Acid Measurement Methods." Anal. Chem., 1979, Vol. 51, No. 14, pp. 2388-2391.

9. Walters, C. L. and J. L. Cheney. "Design and Performance of a Laboratory Sulfuric Acid Generator." J. Air Pollut. Cont. Assoc., 1982, Vol. 32, No. 10, pp. 1058-1061.

10. Cheney, J. L. and C. R. Fortune, "The Present Relationship of Sulfuric Acid Concentration to Acid Dew Point for Flue Gases." Anal. Letters, 1977, Vol. 10, No. 10, pp. 797-816.

11. Lisle, E. S. and J. D. Sensenbaugh. Combustion, 1965, Vol. 36, pp. 12-16.

12. Maddalone, R. F., S. F. Newton, R. G. Rhudy, and R. M. Statnick. "Laboratory and Field Evaluation of the Controlled Condensation System for SO_3 Measurement in Flue Gas Streams." J. Air Poll. Control Assoc., 1979, Vol. 29, No. 6, pp. 626-631.

13. W. R. Dickson. "Comparison of Automated and Manual Sulfuric Acid Sampling Systems." Southern Research Institute, April, 1982.

14. Scaringelli, F. P. and K. A. Rehme. Anal. Chem. 1969, Vol. 41, p. 707.

15. A. A. Taylor. J. Inst. Fuel, 1942, Vol. 16, p. 25.

16. Dietz, R. N. and R. F. Wieser. IBid.

17. O'Keffe, A. E. and G. C. Ortman. Anal. Chem., 1966, Vol. 38, pp. 760-763.

18. Walters, C. L. and J. L. Cheney. IBid.

19. K. Wicker. "SO_3 Determination in Dust-Laden and Dust-Free Combustion Gases." Erdol and Kohle-Erdgas-Petrochemie, 1967, Vol. 20, p. 569.

20. W. R. Dickson. "Comparison of Automated and Manual Sulfuric Acid Sampling Systems." Southern Research Institute, April 1982.

21. Jain, A. K., R. O. Blosser, D. B. Newport, and H. S. Oglesby. "Evaluation and Application of SO_x Measurement Precedures for Kraft Recovery Furnaces." NTTS PB-81-109092.

22. Lisle, E. S. and J. D. Sensenbaugh. "The Determination of Sulfur Trioxide and Acid Dew Point in Flue Gases." Combustion, 1965, Vol. 36, p. 12.

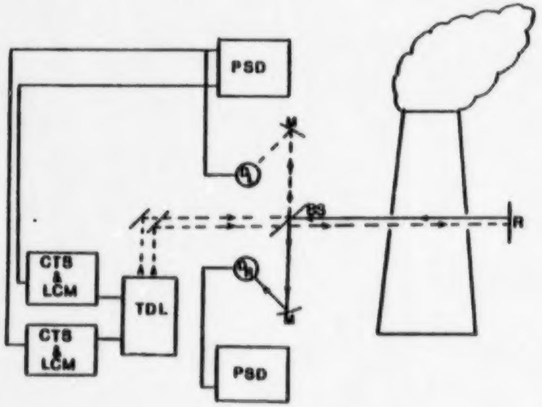
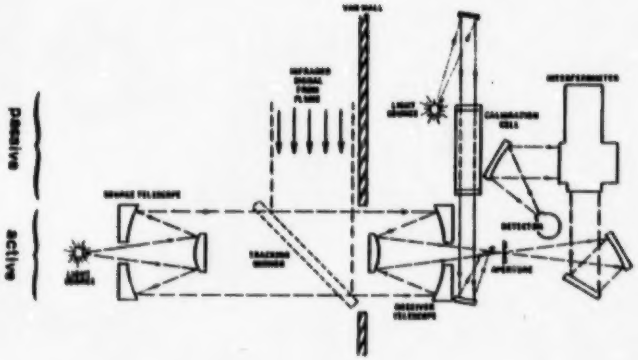
23. Maddalone, R. F., S. F. Newton, R. G. Rhudy, and R. M. Statnick. IBid.

APPENDIX B

SULFURIC ACID VAPOR MONITORING SYSTEMS
SUMMARY OF DRAWBACKS

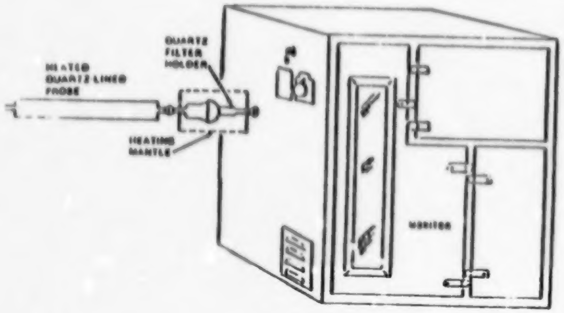
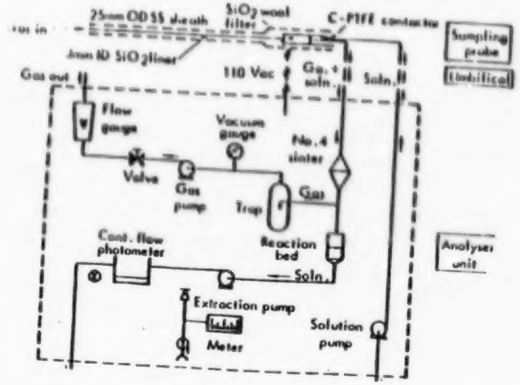
APPENDIX B

SULFURIC ACID VAPOR MONITORING SYSTEMS

Tunable Diode Laser (TDL)	Remote Optical Sensing of Emissions (ROSE)
	
o Not a field instrument. Applicable to laboratory environment only o High technical capability in electronics/computer systems required for operation o Has not been field evaluated o High cost of monitoring equipment	o High technical capability in electronics/computer systems required for operation o High cost of monitoring equipment o Calibration technique requires high technical capability o Not commercially available

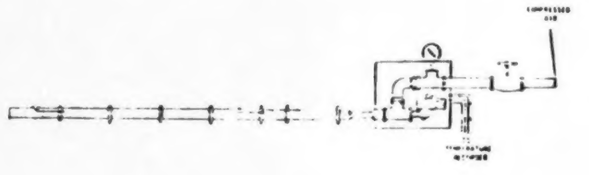
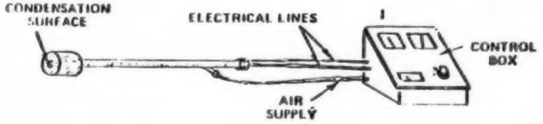
APPENDIX B

SULFURIC ACID VAPOR MONITORING SYSTEMS (Continued)

Sulfuric Acid Mist Monitor (SAMM)	Severn Science Limited Continuous Sulfuric Acid Monitor (SSL)
 HEATED QUARTZ LINED PROBE QUARTZ FILTER HOLDER HEATING MANTLE MONITOR	 Gas in 25mm OD SS sheath SiO2 wool filter C-PTFE contactor 3mm ID SiO2 liner Gas out 110 Vac Gas + soln. Soln. Sampling probe Umbilical Flow gauge Vacuum gauge No. 4 sinter Valve Gas pump Trap Gas Cont. flow photometer Reaction bed Soln. Analyser unit Extraction pump Meter Solution pump
o Requires fulltime attention o Mechanical problems o Not commercially available o Minimum amount of water in flue gas required for sampling (>4%) o Complete rinsing of coil and conductivity cell important o Not a field instrument o Long period to reach equilibrium o Leaks in gas sampling system	o Refractive index of absorbing solution important o Artifact formation causing spurious readings o HCL interference causing SO_2 absorption in isopropanol o Sulfuric acid retention by mist - coalescense system o Flow rate of isopropanol to probe must be constant o Minimum amount of water in flue gas required for sampling (>4%)

APPENDIX B

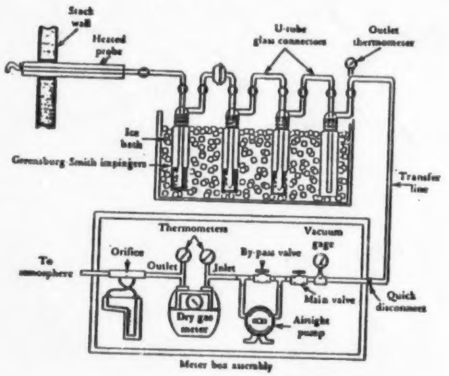
SULFURIC ACID VAPOR MONITORING SYSTEMS (Continued.)

Deposition Rate Probe (DRP)	Acid Dew Point Probe (ADP)
	 CONDENSATION SURFACE ELECTRICAL LINES CONTROL BOX AIR SUPPLY
o Good analytical techniques required o Particulate buildup interferes o Warmup error associated with technique o Limited number of data points.	o Because of Effect of moisture on acid dew point, must take concurrent moisture measurement o Effect of particulate on condensation surface causes erratic readings o Low fuel sulfur can cause abnormally low readings o No sample collected for further analysis

APPENDIX B

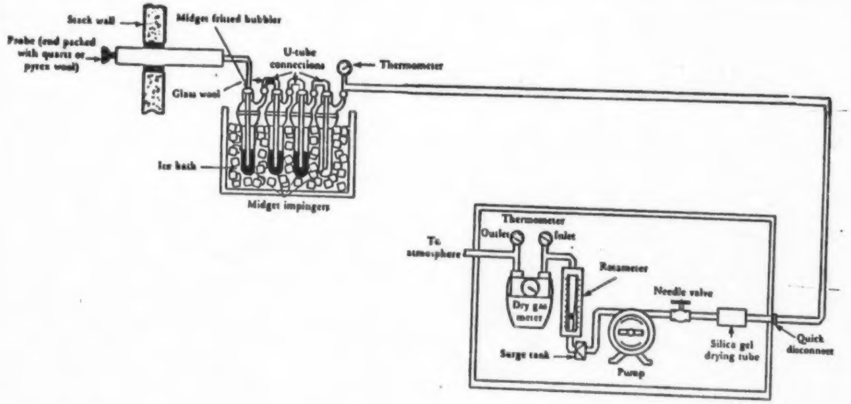
SULFURIC ACID VAPOR MONITORING SYSTEMS (Continued)

Federal Reference
Method 8
(RM8)



- Applicable only to sulfuric acid plants
- Particulate interferences
- Time consuming
- Analytical techniques must be sharp

Modified Federal Reference
Method 6
(MM6)

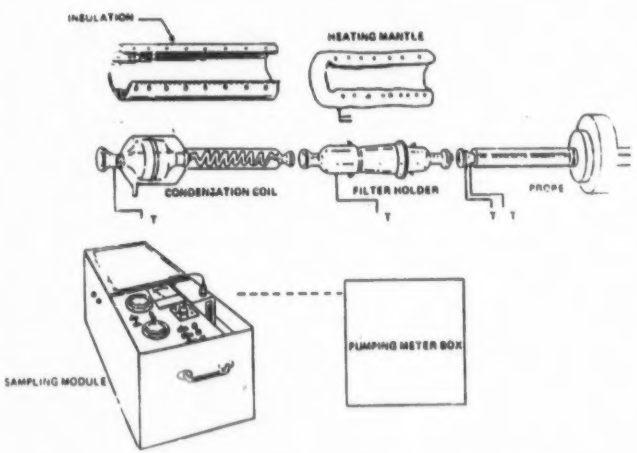


- Artifact formation on probe plug and in IPA impinger
- Poor separation between sulfuric acid vapor and particulate sulfate
- Impurities in reagent grade IPA causing spurious H_2SO_4 values
- Dependent upon sampling rate
- Retention of SO_2 in IPA impinger

APPENDIX B

SULFURIC ACID VAPOR MONITORING SYSTEMS (Continued)

Controlled Condensation System
(CCS)



- o Sulfuric acid condenses on probe
- o SO_2 oxidation by high-temperature filter
- o Sulfuric acid retention by fly ash and filter medium

- o Collection efficiency of condenser
- o Capture of sulfuric acid dependent upon flow rate through condenser
- o Particulate circumvents high-temperature filter and plugs frit
- o Proper diameter of condenser coils important

- o Impurities in reagent grade IPA.